VACUUM PRACTICE

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PREFACE TO ENGLISH EDITION

THE suggestion of an English translation of my book on Vacuum Practice is due to the Editor of the International Text-Books of Exact Science, Professor Andrade. I feel some diffidence in the matter, since there exist already in English several monographs on this subject; in particular, there is Dushman's excellent book, which first appeared in the form of separate articles in 1920.

The French edition of this book, *La Technique du Vide*, was published in 1924 in the *Recueil des Conférences Rapports de Documentation de la Physique*. It was due in large measure to the initiative of M. Debierne that these courses of lectures were given. Their object was to help physicists who had been occupied with military duties to become acquainted with the latest scientific developments. Each course consisted of two or three lectures, and the subject-matter of the courses was subsequently developed and published in monographs. My book was developed from two lectures given in 1922.

My choice of subject was forced upon me by the recent work on high vacua, mainly due to Langmuir and his collaborators. Thus the book owes a great deal to the publications of Langmuir and Dushman, to whom I wish to tender my gratitude and appreciation.

These explanations of the origin of the book are made so that English readers may excuse any lacunæ which they may perceive in it. The book was not intended to give a complete account of the subject, but an account which would be useful to the experimental worker.

From this point of view I wish to draw attention to two additions which have been made. The first (page 56) is a

description of a two-stage condensation pump which I have made, and found to be an improvement on the existing models. The second (page 203) is a note published by Hughes and Pointdexter on the absorption of mercury vapour by the alkali metals. This discovery should still further extend the uses of the condensation pump. It is rather curious that this property of the alkali metals has not been noticed before by the many workers who have experimented with the alkali metals *in vacuo*, especially since, as Hughes and Pointdexter have shown, the absorption can be noticed without the aid of an ionisation gauge.

L. DUNOYER.

PARIS, *29th December* 1925.

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INTRODUCTION

THE great progress made in vacuum technique is due to two causes : first, to the general research on rarefied gases and their behaviour in contact with solid surfaces ; and, secondly, to the great development of certain industries, such as the manufacture of triode valves and of Coolidge X-ray tubes. The undeniable advances made in these branches by certain big American companies is the result of the creation and extension by the companies of their own research laboratories. Although certain results may be criticised regarding their crudeness or their leaving too much to chance when perfect control was necessary, the work from the laboratories of the General Electric Co. at Schenectady, under the direction of Langmuir, and the work done in London, under the direction of N. R. Campbell, have done a great deal towards the improvement of vacuum technique.

The Danish physicist, Knudsen, has also played a very important part. His fine work on the flow of gases which are sufficiently rarefied, for the mean free path of the molecules to be large compared with the diameter of the tube, work which is contained in a series of papers from 1909 to 1911, can justly be considered as the foundation of all subsequent work. Knudsen showed the importance of the study of the impact of gaseous molecules on solid surfaces. This impact may be like either a simple or a diffuse reflection, or the ordinary effect of the twofold process of condensation of molecules on the surface and their subsequent evaporation after a period of time, called by Langmuir the life of the gaseous molecule on the solid surface.

Knudsen's line of argument has also shown the importance of

the interchange of momentum between a gaseous molecule and a moving surface when the pressure of the gas is low.   Shortly after Knudsen's work on gaseous flow came the invention of the Gaede molecular pump, the action of which depends on the peculiar character of these momentum exchanges at very low pressures.   This pump was a great advance in vacuum technique, since pressures sufficiently low for thermionic valves and similar apparatus could be got very much more conveniently, more surely, and more rapidly than with charcoal and liquid air.

In the lectures on which this book was based, owing to lack of time for complete treatment of the subject, it was thought best to give precedence to the very interesting new results obtained relating to the phenomena of contact between rarefied gases and solid and liquid boundaries, these phenomena being very important in vacuum work, rather than to describe pumps and manometers and the processes of elimination and absorption of the last traces of gas.   But in this more complete treatment the logical order would have been a little artificial, because, as is often the case, the progress in technique has not kept up with the theoretical development. Moreover, the study of technique itself, which is the principal object of this book, has taken up so much space that the theoretical treatment has had to be shortened ; so that, although the study of the phenomena is very interesting, it is only dealt with here so far as it concerns technique, but references to papers dealing with the phenomena are given in the bibliography at the end of the book.

The book is divided into four parts, which deal with pumps (Chapter I), manometers and vacuum measures (Chapter II), the building up of tube systems, the elimination of occluded gases, the microanalysis of gases (Chapter III), and, lastly, the production and improvement of vacua by absorbers or electric discharges (Chapter IV).

VACUUM PRACTICE

CHAPTER I

PUMPS

1. **Classification and Characteristics of Vacuum Pumps.** The three essentials for consideration in a vacuum pump are (*a*) the initial pressure from which the pump will work ; (*b*) the limiting pressure it will attain ; (*c*) the speed of evacuation. We shall return presently to the definition and measurement of this speed.

According to the initial pressures from which pumps will work they can be divided into two big classes : those which, taking in gas from a receiver, eject it directly into the atmosphere ; and those which can only work when they eject the gas into a chamber at reduced pressure—a pump of the second class will only work in conjunction with a pump of the first class.

All pumps now used which are rapid and reach very low pressures belong to the second class. Nevertheless, certain types of pumps of the first class are still used, and doubtless will always be used, in spite of their slow speed, because of their simplicity of construction' and operation, because they reach fairly low pressures, and because of the ease with which they can be modified in order to collect the extracted gases.

2. **The Speed of a Vacuum Pump.** In a general way the speed or output of a pump is measured by the volume or mass of fluid extracted per second. In the case of a vacuum pump this is no good as a definition, since the pressure at which gas is removed from the receiver continually diminishes.

The most natural way of defining the speed in this case is to define it as the relative rate of decrease of pressure in a given volume. In order to measure the speed, the pump is supposed to be joined to a manometer by a connecting tube so wide and short that at any instant the pressure shown by the manometer is equal to the pressure in the low-pressure side of the pump. Let p_0 be the lowest pressure to which the pump can reach, and V the volume being evacuated. The speed S of the pump will be defined by the equation

$$S = -V \frac{dp}{(p - p_0)dt} \qquad . \qquad . \qquad . \qquad (\text{1})$$

The dimensions of the speed are those of a rate of change of volume.

From (1) it follows that

$$S = \frac{V}{t_2 - t_1} \log_e \frac{p_1 - p_0}{p_2 - p_0} . \qquad . \qquad . \qquad (\text{2}$$

where p_1 and p_2 are the pressures at two instants t_1 and t_2.

In practice the only pumps to which it is useful to apply equation (2) in order to calculate the speed will be those for which the limiting pressure p_0 is very small. Thus equation (2) is often replaced by the following equation, which is some-times known as Gaede's equation:

$$S' = \frac{V}{t_2 - t_1} \log_e \frac{p_1}{p_2} = \frac{2 \cdot 3 V}{t_2 - t_1} \log_{10} \frac{p_1}{p_2} .$$

(3) is obtained from (2) by treating p_0 as negligible compared with p_1 and p_2. The quantities S and S' are then equal. However, the speed may be defined by (3) without making any stipulation. In that case the speed is no longer the rate of change of pressure in the volume V; but it has in all cases a simple physical significance; it is the rate of change of volume of the gas in the enclosure at any instant, the volume being measured under the pressure attained by the pump at that instant. It is also the volume of gas extracted by the pump in 1 second, measured at the mean pressure obtaining

during that second; because, if in equation (1) we put $p_0 = 0$, we have

$$S' = -\frac{V}{p}\frac{dp}{dt}.$$

If dv be the volume, measured at the pressure p, of the gas extracted from the volume V during the time interval dt, we have, using Boyle's law,

$$Vp = (V + dv)(p + dp)$$

$$Vdp + pdv = 0$$

$$\frac{dv}{dt} = -\frac{V}{p}\frac{dp}{dt}$$

$$S' = \frac{dv}{dt}.$$

Thus when we say that, under a pressure of 0·01 mm. of mercury, the speed of a pump is 1400 c.c. per sec. (the maximum speed of a Gaede molecular pump), we mean that the volume of gas the pump can take out from a sufficiently large enclosure in 1 sec., when the pressure in the enclosure is 0·01 mm. of mercury, is 1400 c.c., measured at that pressure.

Lastly, still another meaning is sometimes given to the speed of a vacuum pump : it is numerically equal to the volume (the volume of the pump being included), in which the pump in 1 sec. will lower the pressure so that the difference between the instantaneous pressure and the limiting pressure will be $\frac{1}{e}$ or 36·8 per cent. of the difference between the initial pressure and the limiting pressure. This follows because, if in equation (2) we put

$$t_2 - t_1 = 1 \text{ sec.}$$

and

$$\frac{p_2 - p_0}{p_1 - p_0} = \frac{1}{e}$$

we have

$$S = V.$$

Also, if in equation (3) we put $t_2 - t_1 = 1$ sec., and $\dfrac{p_2}{p_1} = \dfrac{1}{e}$, we have $S' = V$.

Thus, taking the example given before, the Gaede molecular pump, joined by a very wide and short tube to a receiver of volume 1400 c.c., less that of the low-pressure side of the pump (this volume being very indefinite but small), will, in 1 sec., lower the pressure from 0·01 to 0·00368 mm. of mercury.

3. **Pressure Units in Use.** The C.G.S. unit of pressure is the pressure exerted by the uniform distribution of a force of 1 dyne over an area of 1 sq. cm. It is called the microbar.[1]

This unit is very suitable for the order of pressures met with in vacuum work. The limiting pressures obtained are always lower than 1 mm. of mercury, and sometimes lower than one millionth of 1 mm. of mercury, the lowest pressures attainable in exceptional cases being one ten-millionth of a millimetre ; usually the limiting pressure is of the order of a thousandth of a millimetre. If we express one thousandth of a millimetre in microbars, taking g as 980·665 cm. per sec.[2] we get

$$0\cdot0001 \times 13\cdot596 \times 980\cdot665 = 1\cdot342 \text{ microbars.}$$

So that 1μ of mercury corresponds to 1·342 microbars.

<table>
<tr><td>1 mm. of</td><td>,,</td><td>,,</td><td>1342</td><td>,,</td></tr>
<tr><td>750 ,,</td><td>,,</td><td>,,</td><td>1,006,500</td><td>microbars</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">=1 bar approx.</td></tr>
</table>

And inversely 1 microbar $=0\cdot745\mu$ (approx. $0\cdot75\mu$) Hg.

The pressures will be given sometimes in microbars and sometimes in microns of mercury. When it is merely a question of the order of the pressure obtained, we need scarcely bother to distinguish between these two units.

One of the reasons for the continued use of the millimetre of mercury as a pressure unit is obviously because manometers and especially McLeod gauges, using mercury, are by far the

[1] TRANSLATOR'S NOTE.—M. Dunoyer has used the word " barye " for this unit, which is sometimes called the bar in papers on vacuum technique. Since in England it is the established practice in meteorology to call a pressure of 10^6 dynes per sq. cm. the bar, it has been thought best to translate " barye " by microbar throughout the book.

commonest measuring instruments used in vacuum work at present. It should, however, be noted that there is no difficulty at all in the graduation of McLeod gauges to read directly in microbars. In fact, these gauges have always a mark giving the volume of the compression chamber which is one thousandth of the total volume. If the pressure to be measured is 1 microbar, then the pressure of the gas in this chamber will be 0·745 mm. Hg. So that if the divisions on the graduated tube in direct communication with the chamber requiring evacuation are 0·745 mm. apart (about ¾ mm.), instead of 1 mm. apart, the pressure can be read off directly in microbars.

4. Pumps working from Atmospheric Pressure. Amongst the pumps of this class we shall describe first of all the mercury pumps of the Geissler type (often called Toepler) and the jet pumps of the Sprengel type. These pumps are the simplest to make in a laboratory of modest equipment. They reach fairly low pressures, introduce no vapours other than mercury vapour, and are suitable for gas analysis. The only inconvenience is that they are slow in action, and some of them require continuous attention.

A. Mercury Pumps. *Geissler (Toepler) Type.* A large number of arrangements for obtaining a vacuum have been devised, having for principle the continuous repetition of Torricelli's experiment, the barometric chamber being filled between each operation with the gas to be evacuated. Only one of these arrangements is described below. This one seems to be the most practical and the simplest to make ; it has been used for many years in the Guye Physical Chemical Laboratory at Geneva.[1]

A glass bulb A (fig. 1) is fitted with two barometer tubes B and C, the latter being a capillary tube. At the junction of A and B (a in the figure) a tube G is fused on to connect A to the apparatus which is to be evacuated. The bulb F, whose volume is slightly greater than that of A, is joined to the air-trap E by means of a rubber tube. The working of the apparatus is easily understood from the figure. When the bulb F is lifted the mercury rises first in B and then in

[1] Germann and E. Cardoso, *Jour. Chim. Phys.*, 10, 306–9, 1912.

the bulb A, which is separated from the rest of the tube

FIG. I.
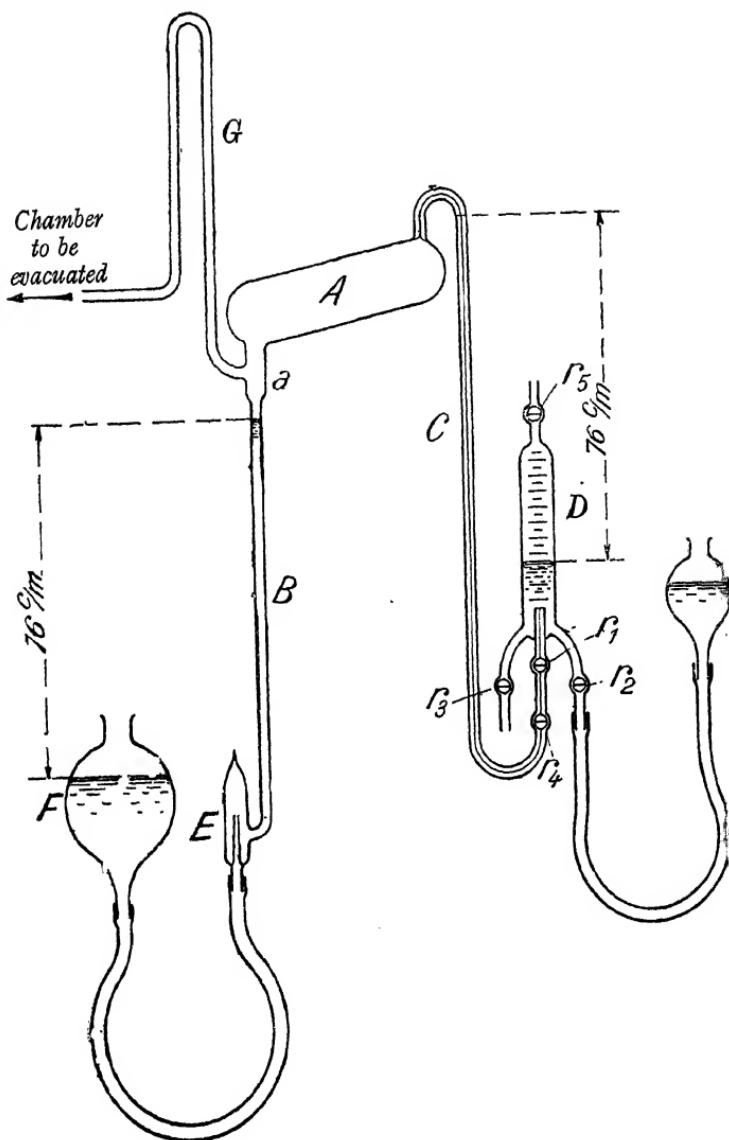
system from the time when the mercury level rises above a.
The gas in A is then swept through the tube C and bubble

into D, which acts as a mercury reservoir. When F is lowered, a vacuum is created in A until the mercury level drops below a. When this happens the gas in the evacuated system expands into A. The operations are then repeated.

It will be noticed that A is inclined so that it can have a big volume without necessitating a big vertical displacement of F. This arrangement also lessens the mechanical shock of the mercury rushing into C when A is full, this rush being very dangerous to the pump. The inclination of A lessens the danger because of the shape of the free surface of the mercury, and also because it is possible to diminish the rate of rise of the mercury level without decreasing the speed of filling the bulb, and, consequently, without diminishing the speed of the pump.

This form of the Geissler pump also gets rid of the operation, so tedious in the older forms, of pouring back into F the mercury driven out by working the pump. This changing of vessels is also a nuisance owing to the fact that the mercury almost inevitably gets dirty in the process. But, with the arrangement of fig. 1, when the mercury level in D is high enough, the level of the column in C passes the upper bend of this tube and mercury flows back through A and B into F.

Lastly, it is very easy to adapt this type for gas analysis, because C leads into a graduated tube furnished with taps and connections as shown in the figure. When the taps r_1, r_4, and r_5 are open, and r_2 and r_3 closed, D serves as a mercury reservoir and the evacuated gases bubble out through the mercury. But if r_1, r_4, and r_3 are closed, and r_2 and r_5 open, D can be filled with mercury from H; if r_5 be then closed and r_1 and r_4 opened, when the pump is worked the gases are driven into the top of D, whilst the mercury excess passes into H. Next, by closing r_1 again and adjusting the height of H, the gases which have been collected may be brought to any desired pressure and passed through r_5 to any other apparatus. The tap r_3 allows a measured volume of gas of known constitution to be passed into D. Finally, it is possible to take the collecting cylinder D right away from the pump by cutting the tube between r_1 and r_4.

This apparatus can be mounted on an iron stand. I
very easy to give it a thorough cleaning throughout.

The bent tube G should be long enough to allow of suffici
mercury pressure to make the flow through C fairly raj
This slightly increases the volume of the tube system,
it gets rid of the ground glass valve so often used with Toej
pumps, introduced as an improvement, but which often sti‹
As the speed of the pump is always small the increase in len
of G is not a grave disadvantage.

For pressures not too near the limiting pressure, the sp
(measured according to Gaede's definition) is got from
volume of the bulb which is alternately filled with merc
and evacuated, and from the frequency of this operati
The increase in volume of the gas, measured under
pressure obtaining at the end of each operation, is equal
the volume of this bulb. As an example let us take
volume of this expansion bulb as 500 c.c., and let the tim‹
a complete operation be two minutes. The mean speed
the pump will be $\frac{500}{120} = 4\cdot17$ c.c. per sec. These numt
correspond to the usual dimensions in practice.

When the limiting pressure is approached experim
shows that the speed decreases. Even with a tube syst
which is not only without leaks, but also with all surf
films of gas driven off, the existence of this limit seems to
imposed by the necessity of keeping the diameter of C fai
large, in order that the time of a complete operation n
not be too long. If the gas caught in A, and forced into
capillary, does not form a bubble wide enough to fill the cr‹
section of the tube, it is not forced through C by the mercu
and when F is lowered the gas returns to the tube system

With this type of pump, although the action is slow, it
easy to get down to 1μ of mercury. The pressure lim
according to published measurements, seems to be betw‹
$0\cdot05\mu$ and $0\cdot01\mu$ under the best conditions. The followi
figures are given by Scheel and Heuse.[1] The evacuat
vessel had a volume of 6 litres and the pump was work

[1] Scheel and Heuse, *Zeitschr. f. Instrumentenkunde*, 29, 47, 1909.

every four minutes (two minutes working and two minutes for equalising the pressure in the different parts of the tube system). The third column gives the speed S', calculated by Gaede's formula,

$$S' = \frac{2 \cdot 3 \times 6000}{60t} \log_{10} \frac{p_1}{p_2}.$$

t (minutes).	p in μ Hg.	S' c.c.
0	64·5	
		4·0
12	39·9	
		3·8
24	25·4	
		3·6
48	10·7	
		2·5
60	7·09	
		3·6
108	1·41	
		3·5
120	0·93	
		2·2
180	0·24	
		3·9
192	0·15	
		2·2
240	0·053	
		2·8
252	0·038	
		1·4
264	0·032	
		0·7
300	0·025	

One of the disadvantages of the type of pump is the constant manipulation required. This can be avoided, though the apparatus is of course more complicated, by using a water pump which lifts the mercury automatically, has been done by Pamfil.[1] The automatic method of lifting mercury is described further on.

[1] Pamfil, *Jour. Chim. Phys.*, **11**, 801-4, 1913.

Sprengel Pumps, called Mercury Jet Pumps. Until th appearance of the Gaede rotary mercury pump, mercur jet pumps, of which Sprengel's was the first model, wei used to reach the lowest pressures. The name jet pumj although usually given, is incorrect, and there is no similarit between the action of this pump and that of the water j(pump. The working of the latter depends on the speed the liquid surface, the viscosity of the gas (owing to whic it is drawn along), and the form of the nozzle from which tk jet expands and, striking the walls, stops the bubbles of which were drawn along from getting back. In this type mercury pump all the mercury does is to cut off a successic of bubbles in a vertical tube, and the bubbles remain apa if the tube be sufficiently narrow (1 to 2 mm. diameter), tl bubbles of gas being shut in between short columns of me cury. If the lower end of the tube is placed in a bowl mercury and the upper end joined to a bulb containing rarefied gas, the height of the column is such that the tot length of mercury in the column is equal to the differen between the barometric pressure and the pressure of t rarefied gas, when both these pressures are expressed mercury heights. The fall of a fresh drop of mercury on t hole in the top of the tube encloses another bubble of gas the tube and forces the whole string of drops downwɛ and diminishes the pressure in the receiver.

For many years these pumps were the only kind use(the evacuation of X-ray tubes, and they are still usefu the laboratory on account of the simplicity of their const tion, in spite of the complication of certain types which supposed to embody improvements. It is also easy collect the evacuated gases from this pump. It can started from atmospheric pressure, but it is better to start reduced pressure, which can be easily got by using a fil pump. In this latter case the pump has the advantage ov the usual Geissler type in that it functions continua without the attention of an operator, owing to the automa lifting of the mercury.[1]

[1] The method of lifting the mercury automatically has been used for y(in chemical laboratories, the method being called Verneuil's method.

Fig. 2 shows a simple model of this type of pump. The apillary tube AB, about 125 cm. long and of internal dia-
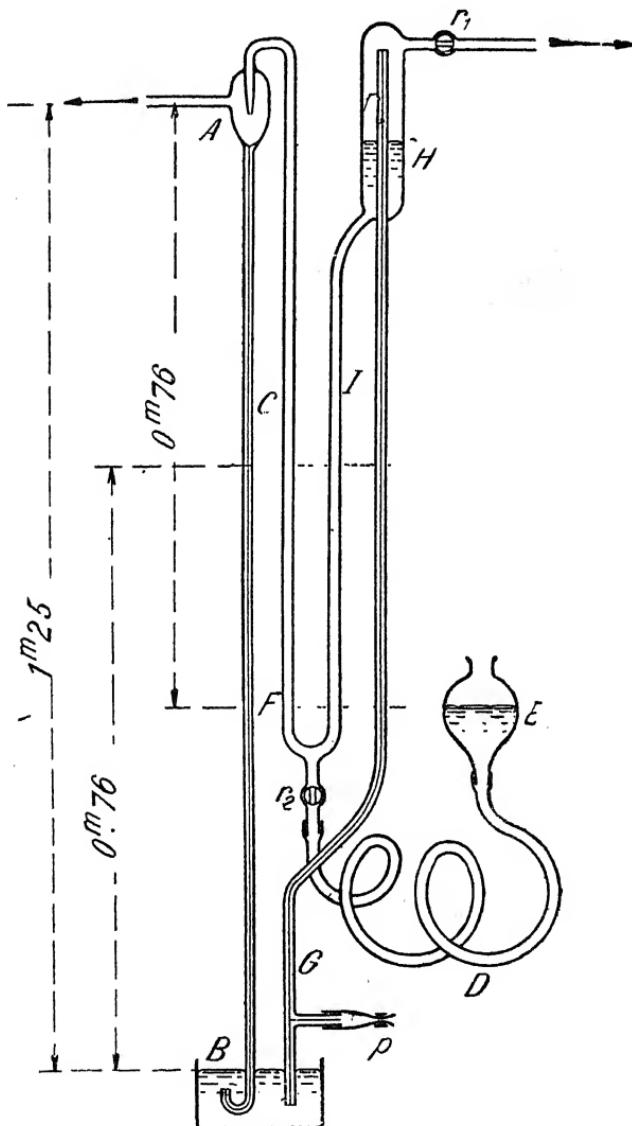
FIG. 2.

eter 1 to 2 mm., ends at the top in a small bulb which is direct communication with the bulb requiring evacuation,

and the nozzle is fixed inside the small bulb. It is not ver
important to have the jet vertically above the end of th
capillary. The nozzle is joined through C, and a rubber tub
D to the reservoir E. If the reservoir is lifted a little abov
the level of the jet, drops of mercury begin to fall and evacua
tion begins. The working ceases when the difference of leve
between the jet and E is equal to the difference between th
barometric height and the gas pressure in the receiver.
must therefore be longer than 76 cm., and then air will no
get back into A so long as the level in E is above F.

When the flow of mercury stops, some mercury must
poured from B into E. This is very inconvenient, and c
be avoided by using a filter pump or any similar pump which
will only get down to 2 or 3 cm. of mercury, but has a big
output. The apparatus is then a little more complex. The
water pump is joined to a bulb H, which is about level with .
A capillary tube G penetrates into H, and has its lower er
in the reservoir B. Near the bottom of G a side tube is l
in, on which a short piece of rubber tubing P is fitted, tl
rubber tube being nearly closed by a clip. The air whic
gets in at this leak breaks the ascending mercury into dro
so that it will reach up to H, where the air bubbles are
leased. The mercury flows down into I, and through C
the jet.

If the water jet is stopped without closing the tap r_1,
mercury in I drops to the level F, and the pump stops worki
and sometimes air gets into the vacuum chamber. If
water pump is started again, the mercury again rises in
and falls through I, but some air bubbles may be caught in
To stop these from getting into the vacuum chamber th
reservoir E is used. The tap r_2 is opened, and E is raise
until the bubbles are driven into H. The tap is the
closed.

The extra reservoir E is also useful when the pumping
started. If r_2 is opened and E lowered, H can be put
direct communication with the evacuation chamber. Th
tap is then closed and the water pump started. As soon a
the mercury from G begins to flow into H, the tap is opene
again and E is raised to clear out the bubbles, as indicate

bove. When this is effected the tap is closed and the pump
arries on automatically.

The pump which has just been described can be made by
nyone with a knowledge of the rudiments of glass blowing;
anyone who wants to do vacuum work unaided this know-
edge is indispensable. However, Guichard [1] has given a
model which can be made without a single glass joint.

The capillary tube AB (fig. 3), in which the drops are
prmed, passes through the stopper K into the wide tube C,
hich is a little longer than the barometric height, and, at
upper end, is joined to the vacuum chamber. K fits into
wider tube D, which acts as a mercury reservoir. The
nercury flows from E through F, the flow being regulated by
pinchcock G on a rubber tube. If the initial pressure is
tmospheric, D must be filled up to the level of the hole a in
he wall of the capillary, in order that the drops may begin
fall into B. When the vacuum is established only a small
nount of mercury is left above K. The capillary is bent
ck at the lower end, so that the gases can be collected above
mercury in H, and the mercury overflow from the latter
ses into I and can be poured back again into E.

his pump is very simple and works very well. It is very
at the start if it begins from atmospheric pressure, but
cond opening can be made so that it can be used with a
er pump. The pump also needs an operator to pour the
cury back into E, but it is easily modified to avoid
s.

Fig. 4 shows an improved form, also without glass joints.
e capillary tube B passes through a stopper K in an up-
rned bell-shaped tube which is connected to the vacuum
amber. The mercury drops fall from a small sideways
le a. The mercury flows through the U tube C, leading
m the short bell tube H, which is joined to a filter pump
lich raises the mercury from the lower reservoir through G,
ing an air leak p as before, but made by having an imperfect
bber joint. Since the pressure, when the vacuum is estab-
hed, is the same on both sides of the stopper K, there is no
nger of a leak there.

[1] M. Guichard, *Bulletin scientifique trimestriel*, 3, 1911.

PUMPS

With any of these arrangements it is easy to join gas collecting apparatus on to the bent-up end of the capillary Fig. 1 gives an example of this.
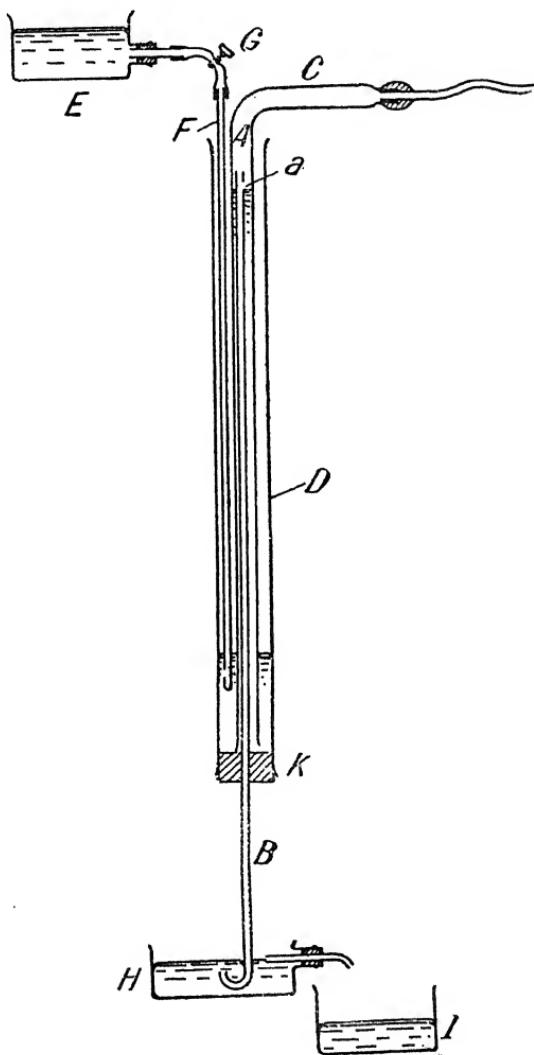
FIG. 3.

With pumps of the Sprengel type quite low pressures be reached. Kahlbaum gives the following results obtair in evacuating a 500-c.c. bulb. In twelve minutes the pressu

hanged from 500μ to 0·165μ, and in twenty-seven minutes to
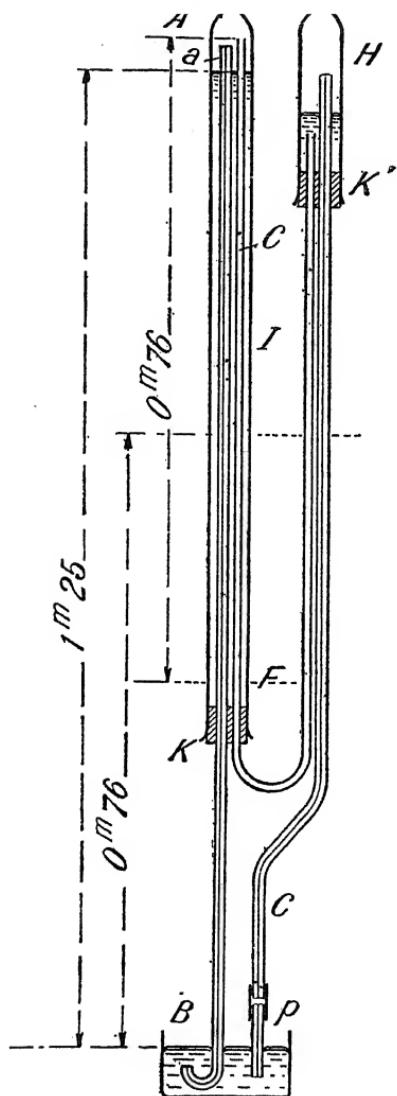
FIG. 4.

7μ, which correspond to speeds of 5·5 and 0·47 c.c. respec-
vely. The low-pressure limit is said to be 0·002μ, but

$0 \cdot 1\mu$ is more usual even under the best conditions which c̲ be ordinarily obtained.

It should be noticed that, in order to get down to very lo̲ pressures, the capillary tube down which the mercury drop should have a very small cross-section, because, if this is no̲ so, below a certain pressure the mercury drops will no longe̲ cause the formation of air bubbles. But the reduction ir̲ cross-section reduces the speed of the pump. A low limitin̲ pressure necessitates a small output.[1]

B. Oil Pumps. *Piston Pumps of the Geryk Type.* The̲ pumps are very convenient on account of their durabilit̲ and their fairly high speed, and are easy to work by han̲ since the stroke frequency is suited for this. A single-cylind̲ pump readily gives a quarter of a millimetre ; a two-cylinde̲ pump (cylinders in series) gets down to one-tenth of a mill̲ metre. These pumps look rather like the old Bianchi pump̲ but they are an improvement on these, being more simpl̲ and getting down to lower pressures on account of the elimin̲ tion of harmful clearance spaces. These pumps are v̲ useful in chemical laboratories.

Fig. 5 gives a model described by Barton.[2] The tub̲ connects the apparatus to be evacuated with the ann̲ space B, at the lower part of which a hole T opens into̲ pump cylinder C. The piston D, fitted with a hydr̲ leather washer E, is covered with oil. When the pisto̲ lifted it closes the hole T and compresses the air in C ̲ the valve F is lifted and the air passes into the upper chan̲ G. The lower part of G is also filled with oil, and this m̲ with the oil lifted up on the piston head, and the air bub̲

[1] Reasons have been given above for the inclusion of descriptions of simple types of Geissler and Sprengel pumps, in spite of their slowness̲ action. Before the invention of the Gaede mercury pump a number different types of mercury pump were designed with the idea of increas̲ the speed. These have now only a historical interest. One of the m̲ remarkable was Moulin's mercury pump, which is still used in some factor̲ and which gets down from atmospheric pressure to $0 \cdot 01$ mm. in four minut̲ working on a 1-litre vacuum chamber. For a description see *Bulletin de̲ Société Française de Physique*, p. 73, 1910.

[2] E. H. Barton, *An Introduction to the Mechanics of Fluids*, p. 197. Fi̲ is taken from a series of articles by Dushman on " The Production ̲ Measurements of High Vacua " (*Gen. Elect. Rev.*, 1920 and 1921), from wh̲ many extracts are made in this book.

ough the oil.   When the piston drops again a spring closes
valve F, which separates the two oil baths.   A vacuum
created in the cylinder C until the hole T is uncovered, and
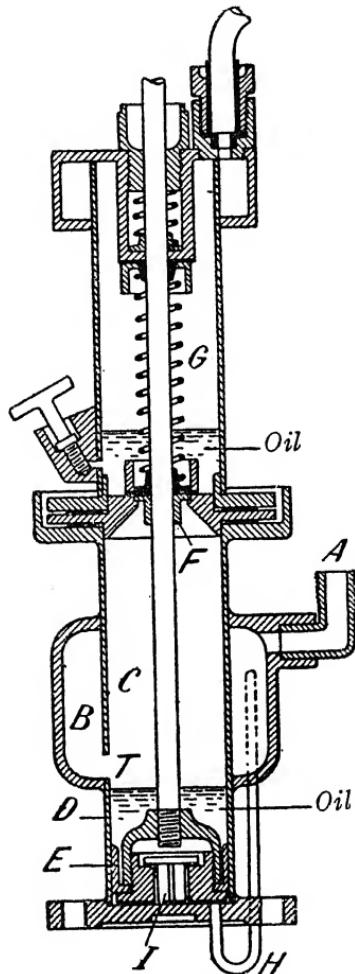
FIG. 5.

the action begins again.   The tube H joins the annular
B to the bottom of the cylinder and prevents the piston
ι sticking there.   The top of the piston rod is linked to the
of a beam which gets a vertical motion from a wheel with
εccentric link.

2

Rotary Pumps with Toothed Wheels. These pumps, wh..e'er
have only come on the market during the last few year th
have been evolved from the oil-circulating pumps which a.w.b
used with internal combustion engines, and more particularb.v
with aircraft engines. Taking up very little space, silent, an.a
with a big output, these pumps are the most useful yet ma.eve
if the limiting pressure required is about 1 mm. When th.rh.
are new they easily get down to one-tenth of a millimetre, bu. (
and this is perhaps their principal defect, the fairly rap.aq
wearing of the cogs soon raises the limit to several millimetr.
After running for 1000 hours, the limit is still 5 or 6 m.
This is quite good enough for the fore vacuum of a Ga.e.
mercury pump, but it is far too high for a molecular pump .
a condensation pump.

Fig. 6 shows a single-stage pump of this type. The tooth.
wheels *E* and *F* are carefully set inside a case made up of
bottom *A* and a cover *B*, through which passes the axle.
which turns the wheel *F* ; *E* is free on its axis and is turn.
by *F*. At *K*, where the cogs are just disengaging, a be.
tube *G* passes through the bottom of the case *G*, being.
communication with the apparatus requiring evacuat.
Opposite *K*, at the place where the cogs engage, a tube.
communicating with the outside, passes through the cov.
The whole case is immersed in oil.

When the wheels turn in the sense shown by the ar.
the volume available for the gas at *K* continually incr.
as the teeth separate.

The gas occupying the volume *a* between two cogs is ca.
a moment later in *b*, between the same teeth and the si.
the case, and stays there until *b* comes opposite *H*, wher.
accumulates and escapes by the tube. The immersio.
the whole in oil stops any leaking in of the external
Lubrication of the moving parts is automatic, owing to
atmospheric pressure exerted through the hole *L*. The d.
of oil which are carried up *H* fall back into *J*.

A much lower pressure can be reached if two or three
of cogs are put in series. The pumps on the market are n.
in this way. The cover *B* of fig. 6 is replaced by a se.
box similar to *A*, the bottom of the box being pierced b.

ined hole, so that the delivery pipe K' of the first pair
ls into the suction end of the second pair. Above the
ond box the cover B is fitted, which carries a sleeve for the
ating axle.
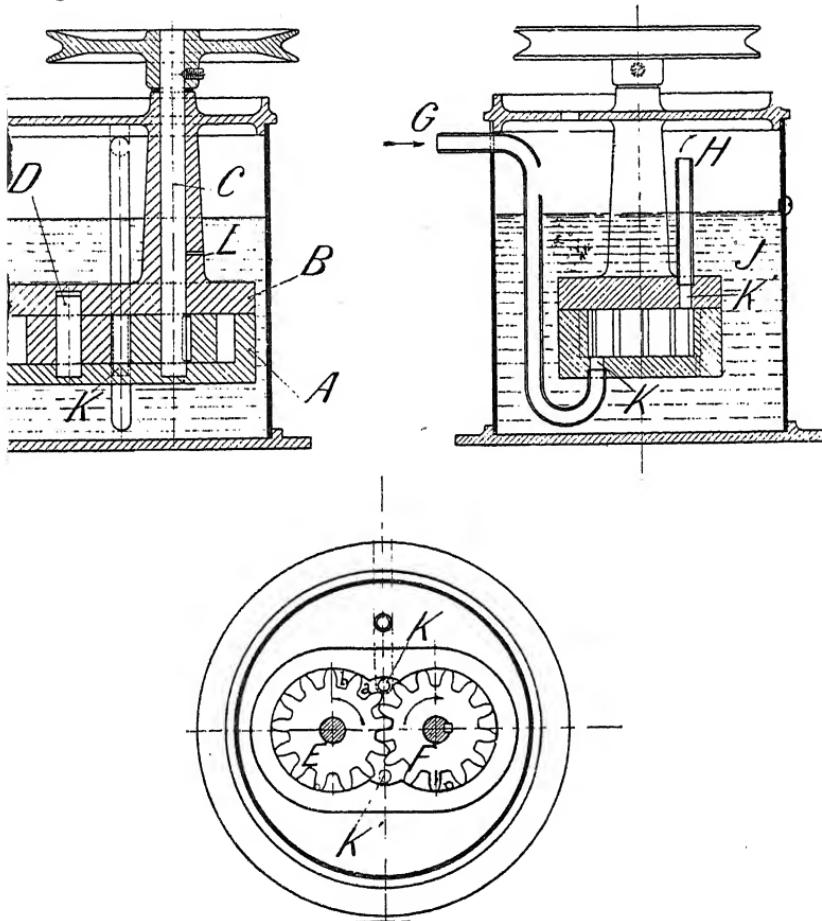
FIG. 6.

he usual speed of these pumps is from 800 to 900 revs.
minute. A little electric motor of $\frac{1}{8}$ to $\frac{1}{6}$ H.P. is suitable
driving one. As the fitting must be very close, there is a
lency to warm up. It is very important to avoid this,
the limiting pressure rises when the pump is warm,
bably owing to expansion and to variation of viscosity of

the oil, which should be neither too thin nor too thick.
thus better to have a double-walled container for the pump,
run cold water through the jacket.

Note on a Useful Precaution. Sometimes with this type
pump the oil gets into the evacuated tubes. This trou
usually starts when the pump is stopped and oil oozes slo
into the tubes, unless the operator is on the look out.
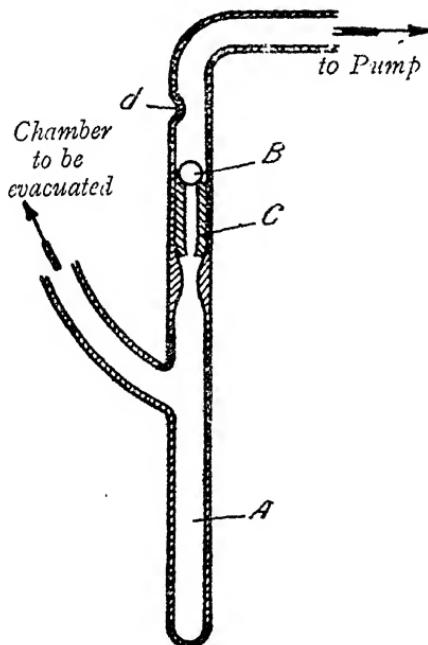
FIG. 7.

This penetration of oil can be stopped by placing a
valve between the tube system and the pump ; the
may be of a type which is also useful with a filter pun
stop the water from sucking back when the pressure
supply diminishes.

The valve is simply a small ball *B* which rests on the
of a short piece of rubber tubing *C*, the latter being a tigh
in a glass tube which is joined to the pump. A constric
in the glass tube stops the rubber tube from sliding.
movement of the ball is stopped by a little re-entrant hum

ich is made after the ball is put in by pressing with a point
the side of the tube when the latter is heated sufficiently.
ien air gets in from the pump side the ball is pressed tightly
o the rubber, and the oil (or water) can only leak through
slowly. The small quantity which leaks in is collected
ue tube *A*, and does not get into the apparatus which is
:uated. (In the case of a filter pump working under in-
cient pressure, the air rush is not continuous, and the
'e need not be as perfect as in the case of the oil pump.
water pump can be left running all night if the tube *A*
eplaced by a fairly large reservoir of volume about 250 c.c.)
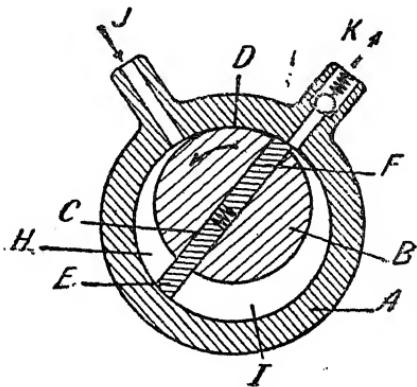
Fig. 8.

)all-bearing or a bronze ball will do for the valve ; it is
:ter still to use a glass ball, which can easily be made suffi-
.ntly round and regular.

Rotary Pumps with Vanes. *A* (fig. 8) is a fixed cylinder
)sed at the ends by flat plates through which passes an
;entric axle made in one piece with the cylinder *B*. This
nder is always tangential to the inner surface of *A* along
: generator through *D*. It is cut through across a diametral
ne, and in the hole *C* slide two vanes *E* and *F*, which are
)t apart by a spring which presses them against the walls
the cylinder *A*. This cylinder is pierced by two holes,
and *K*, for suction and expulsion. Owing to the rotation
B the chamber *H* increases in volume, whilst *I* diminishes.
ie gas is taken in at *J* and exhaled at *K*.

Pumps working on this principle have been used for ma
years for transferring liquids from one vessel to anoth
There are also pumps of this type which are used for co
pressed air which are handy, strong, and quite roughly (
together, the paddles being of hard wood and the centrif
force being quite enough to keep these pressed against
outer cylinder without the aid of a spring. Gaede seem
have been the first to use this idea for vacuum pumps.
these the fitting must be very exact, and lubrication is
important : the ends of the vanes should slide over a
tinuous layer of oil covering the inner surface of the cylind
Moreover, in order that there shall never be a big differe
of pressure between the two faces of the paddles, a valve m
be placed in the exit pipe K so that the pressure in I is
atmospheric. In order to stop air leaking in along the
oil is dropped continually on to it by means of a ring of wh
the bottom dips into an oil bath contained in the cas
which is cast in one piece with A.

The oil leaks slowly into the pump, and is driven out thro
the valve at K, and falls back into the oil bath in the cas

A new pump of this type, working well at 500 revs.
minute, gives a limiting pressure of from 0·01 to 0·02
The limit rises fairly soon towards 0·1 mm.

The working of a pump of this type can be very
improved by (1) putting it in series with another pun
the same type ; (2) immersing it completely in oil, w
also simplifies the construction.

Fig. 9 gives a diagram of the mounting. A is the int
and the mixture of air, and oil is pushed out through the va
R'.

This latter arrangement is now the most common
incandescent lamp factories. Three pumps in series can
down to 0·1μ with an output which is still useful. Bes
which, when the pressure rises to a few millimetres of merc
the output becomes enormous. This is obviously a g
advantage in a lamp factory, where the replacement
set of lamps on a rack often brings part of the vacuum sys
up to atmospheric pressure. The limiting pressure of o
which is very remarkable considering the mechanism of

ımps, can only be reached by a set of pumps which have
en working for some time and under such good conditions
at the rubbing parts have worn to a perfect fit without
ratches.   The following table (p. 24) is given by the firm,
iffe-Gallot et Pilon, for a double pump of this type evacuat-
a 10-litre receiver.   The last column gives the speed of
pump calculated from Gaede's formula.   The abnormal
put between 48·1 mm. and 0·12 mm. is no doubt due to
fact that these pressures are very far apart, and that
working of the pump (circulation of oil, mixture with
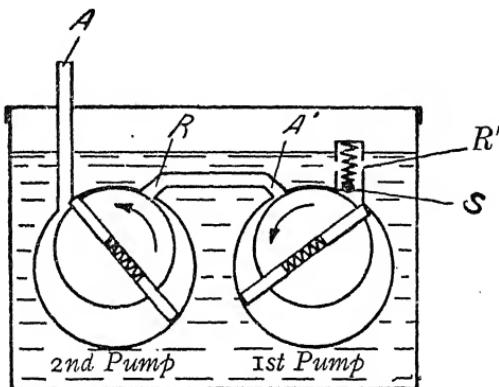
Fig. 9.

workiィg of the valve) changes rapidly between these
essures.
Before leaving this subject we shall briefly outline the
ktraordinary construction of the American Trimount pumps,
lsọ with paddles, which seem to be used a good deal in
merican laboratories.[1]   One disadvantage of the mounting
scribed above is that the intake *J* and the outlet *K* are
parated by the contact along a single generator of the
volving cylinder and the outer case.   Very little wearing
: this contact puts the two tubes in connection when the
ıddles are horizontal.   This disadvantage can be got rid of
y increasing the number of paddles so that there is always
paddle between the two tubes.   But with paddles worked

[1] See, for example, MᶜLennan's work on spectroscopy in the extreme
ltra-violet.

with springs the construction would become rather complicat
It is also obviously better to replace contact along a sin
line by contact along an arc giving a much larger area of co
tact.   These two improvements are contained in the Trimou
pump.   Fig. 10 gives a rough idea of its construction.

Time in seconds.	Pressure in mm. Hg.	Speed in c.c. per second.
0	760	125
30	522·7	202
60	285·4	592
90	48·1	1990
120	0·12	366
150	0·040	327
180	0·015	485
210	0·0035	112
240	0·0025	13·6
270	0·0024	14·2
300	0·0023	14·8
330	0·0022	15·5
360	0·0021	16·2
390	0·0020	

The inside of the body of the pump A consists of t
eccentric borings, one of these being centred on the axle
which is made in one piece with the cylinder C, through t
walls of which grooves, such as D, are bored.   Fitting close
in these grooves are the paddles E, each made of several ste
laminæ which are not pinned together.   To ensure conta
between the paddles and the outer case a cylindrical ring
is threaded on to the axle B, and this ring is kept in conta

th the inner wall of A by means of the roller G, which
urns freely on an axle H, which is in one piece with the
mp body. Thus when the drum C rotates the ring F
so rotates, either with or without slipping. The external
ameter of F is such that the paddles are pushed into contact
ith the lower boring A' when their inner ends come into
ntact with the ring, by sliding in their grooves. The
lique contact at the surface of the ring is allowed for by
slipping of the thin steel laminæ over one another.
certain periods of the rotation the contact is linear.
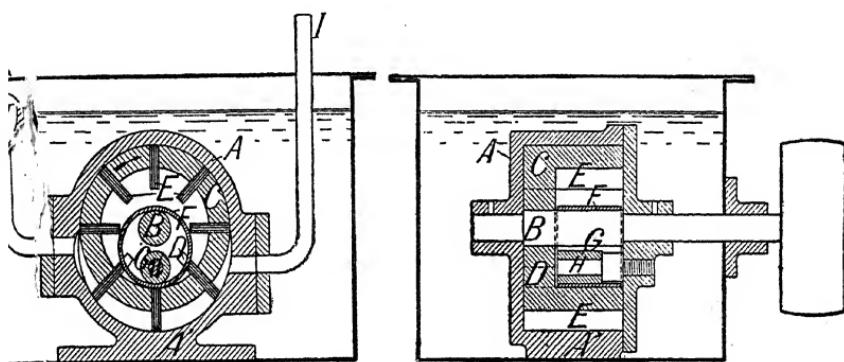
FIG. 10.

If the pump is examined when the axle is being rotated
slowly, it is seen that there is continued contact without any
play. The intake is at I and the expulsion at K. Generally
two pumps are coupled in series inside a single oil bath,
and the oil-bath container is exhausted by a third pump.[1]

[1] Instead of putting the paddle inside the rotating cylinder, as in the models
described above, it may work in the stationary outer casing. This has been
done in a pump called the Cenco Hyvac, which has just been put on the
market by the Central Scientific Company. Fig. 11 gives a diagram of the
pump and shows its action.

A spring D keeps the paddle in contact with the rotating cylinder, the
paddle sliding in a groove in the outer casing. The rotating cylinder A is
eccentric and keeps tangential to the inner wall of the outer case. The
intake is at E, and the expulsion at L through a valve. The whole pump is
immersed in oil, and allows two similar pumps to be placed in series in the
same outer case. A special valve on the intake tube stops the oil from getting
into the tube system when the pump is stopped, so long as a vacuum has been
established.

According to information published by the makers from tests made at the

5. **Pumps needing a Fore Vacuum.** The pumps descri‸
the present can all be worked between atmospheric
and quite low pressures. They are only put in se₁
a lower pressure limit. The pumps which wilⅼ
described will only work from a reduced pressure, so ‸

University of Illinois, the low-pressure limit of these pumps is lo
1μ (0.85μ for one pump and 0.50μ for another) under the best conditi꜀
output is quite small at low pressures, as will be seen from the tabl
The wonderful improvement in the limiting pressure seems to be due
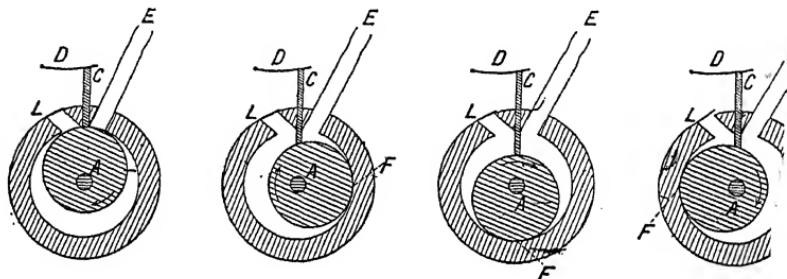
FIG. 11.

to the different mechanical arrangement, and particularly to the fact that the
very thin film of oil between the surfaces of the two cylinders at F is con
tinually renewed just as the cylinders come into contact. The single ᴎꝛddle
is also well placed for lubrication. The table gives the results g᷄ᴏᴄ with ꜳ
pump of this type making 225 revolutions per minute and evaꜯ꜀u᷄in᷉ ᴀ
13-litre vessel. The speed is calculated from equation (1).

Time in minutes.	Pressure in μ Hg.	Speed in c.c. per sec.
30	7.86	
35	3.40	161
40	2.00	123
45	1.58	70
50	1.39	46
55	1.31	24
60	1.19	46
65	1.17	9
70	1.15	10
80	1.09	18
90	1.00	33
100	0.98	10
110	0.94	26
120	0.92	17
130	0.91	10
140	0.90	12

must always be put in series with a fore pump, that is a pump working between the reduced (fore vacuum) pressure and the atmospheric pressure.

A. The Gaede Rotary Mercury Pump.   This pump is now so common that a short description of it will be sufficient. Fig. 12 shows how it works.   For the sake of clearness the porcelain drum is drawn with only two partitions, although there are generally three.   The partitions are marked $m_1z_1t_1$ and $m_2z_2t_2$.   The diagram on the right is a section through xx perpendicular to the axis of rotation, whilst the left-hand diagram represents a section containing the axis of rotation.
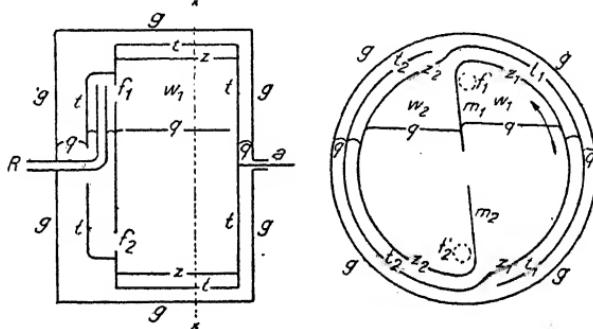
FIG. 12.

The drum is enclosed in a thick metal case g, through which axle passes at a, through a stuffing-box with a mercury The pressure in the case is lowered to a few millimetres. The bent tube R, which penetrates inside the drum, is the take of the pump.   If the drum is rotated in the direction own by the arrow, the volume of the chamber w_1 increases, rl gas flows into this chamber through the hole f_1.   A ierence of level is produced between the mercury in w_1 d the mercury in the outer case.   When the hole f_1, as the tation proceeds, passes below the mercury level, as f_2 is the diagram, the chamber w_2 is cut off from the outer case. he volume of this chamber is continually decreased until smmunication is again established with the envelope by the annel between the partitions z_2 and t_2.

It is worthy of notice that the gas extracted by one operation in w_1 or w_2 is put in communication with the high-pressure

side without being reduced to a small volume.   This is p[?]
ably one of the reasons for the much lower limiting pres[?]
reached by the Gaede compared with other mercury pun
The limit is from 0·01μ to 0·005μ under the best poss
conditions.   In other pumps, when separation is perfori
either by filling a bulb, or by the fall of a drop of merci
the gas is only pushed along if it forms a large enough bub
When there is very little gas left, the volume of the bubl
is small and they stick to the sides of the bulb or fall t
either owing to surface tension or adsorption on the g
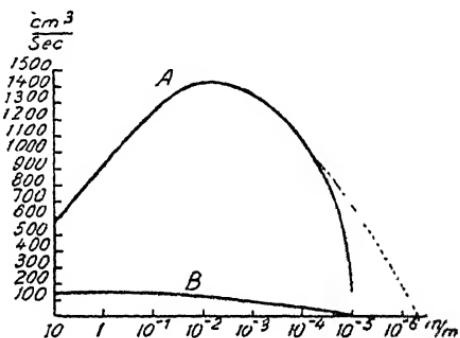
FIG. 13.

surface.   The gas is released again when the bulb is empti
or, in the other case, in the time between the fall of two dr[?]
The other reason why the limiting pressure of the Ga
is so much lower than that of other liquid mercury pumps
because it is so much faster, owing to the rate of incre
of volume of the chambers marked W.   Since the limi[?]
pressure is reached when the quantity of gas removed in
time interval is equal to the amount coming from the v
during the same interval, it is obvious that increasing
speed of a pump which works by the mechanical increas[?]
a volume means lowering the pressure limit.
The line B of fig. 13, in which the abscissæ are the value[s]
$1 + \log \dfrac{1}{p}$, gives Gaede's own measurements of the spee[?]
one of these pumps.
The usual connections of the pump are shown in fig.

with a cut-down manometer to show when the fore vacuum pressure is good enough to let the pump work.   This pressure should not exceed 10 mm. of mercury.   If the water pressure is high enough a filter pump will get down far enough.   A valve, of the type already described, should be used with the
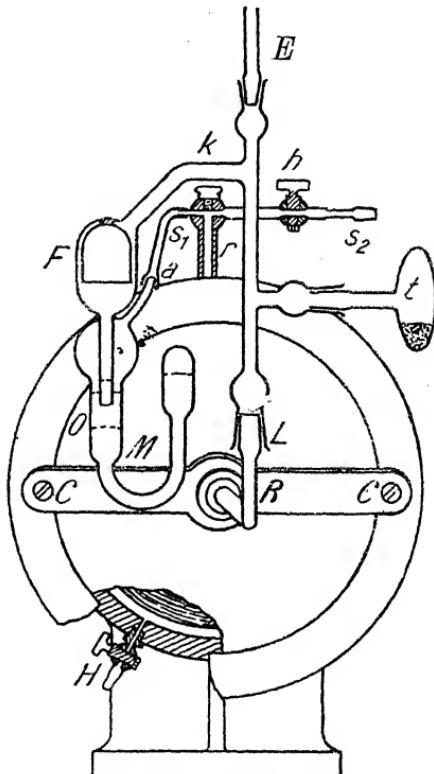
FIG. 14.

r pump.   As the Gaede pump is usually delivered for ratory work, it has three ground joints: one at E, one at and one for the small phosphorus pentoxide bulb t.   Even hese joints are good joints it is always best to cut down the nber as far as possible, in order to avoid gaseous hydrobons, and also the chances of a leak, which sometimes pears after several months' running.   The ground joint E can obviously be got rid of.   The ground joint for t be cut out at the cost of having to cut the tube each

time fresh pentoxide is required. The ground joint at L can also be dispensed with. It is rare to find that the low-pressure side of a Gaede does not leak a little, and it is usually necessary to put a tap between the pump and the vacuum apparatus in order to avoid the effect of communication between the low- and high-pressure chambers of the pump due to the falling of the mercury level below the axial hole. The tap itself, however, is often a source of trouble. Leaks often occur also at the rubber ring through which R passes to the pumps. By replacing the metal tube by a glass tube of the same shape, cemented through the glass front (which is easily ground round the central hole), it is possible to ha a tube system with all the joints fused. Under these con tions the vacuum will hold up perfectly for days or ev weeks. It is also better to fix on a glass tube in place of rubber tube as_1.

Although this pump will not get down low enough evacuation of thermionic valves, it will probably contii to be very widely used in laboratories in all cases where pressure desired is not less than $0·01\mu$, and when it is necessary to get rid of mercury vapour. This pump is v strong, simple, and convenient, besides which it can stopped at any time without any alteration in the p sure reached. This is not so for the pumps descri below.

B. Molecular Pumps. The action of molecular pumps pends on the fact that the molecules of a gas which str a fixed boundary rebound at random—that is, the mot after impact is independent of the velocity before impac regards both magnitude and direction. Although the ex ness of this law is still debatable, it is certainly very near truth for a gas whose molecules have no motion other t' heat motion, and which do not react with the materia the walls. The action of impact and rebound is equival to condensation on the walls and subsequent evaporati Thus, if the boundary is given a motion of translation in own plane, all the molecules coming off from the bound will be given a velocity component equal and parallel to velocity of the boundary.

Let AB (fig. 15) be a channel cut in a solid wall, and let C be a boundary moving in the direction of the arrow. Owing to the momentum given to the molecules by C, there will be an accumulation of molecules at the B end. For a given value of the velocity of C a constant difference of pressure will be established between A and B, this difference being measured by the manometer M.

If the distance between C and D is large compared with
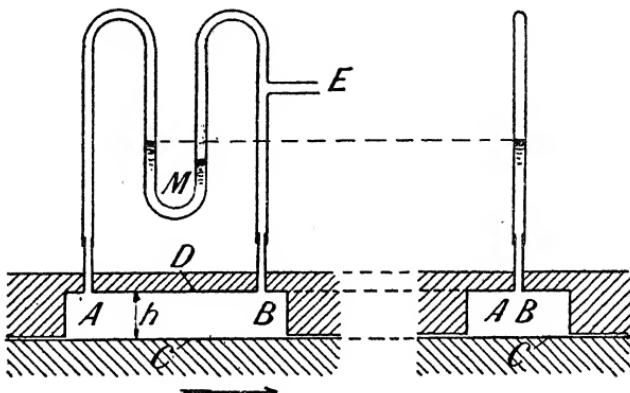
FIG. 15.

mean free path of the molecules, the pressure difference, ⸱rding to the kinetic theory of gases, is given by

$$p_B - p_A = \frac{6\eta u a}{h^2} \qquad . \qquad . \qquad . \qquad (1)$$

⸱re η is the viscosity of the gas, u the velocity of the ⸱ing surface, a is the distance between A and B, and h between C and D. Since η is independent of the pressure, pressure difference is independent of the average pressure ⸱he cavity. Suppose that the pressure difference is 10 mm. ⸱he pressure at E is reduced by means of a fore pump, the ⸱ssure at B will always be 10 mm. greater than the pressure   If the fore vacuum pressure is 10 mm., the pressure ⸱A would be zero. But before this happens the mean free ⸱th of the molecules becomes great compared with h, and ⸱ formula will no longer apply.

According to Knudsen and Gaede,[1] when the mean free path is large compared with h, the ratio of the pressures p_A and p_B is independent of the average pressure. This result follows from the law of flow of highly rarefied gases, which was first given by Knudsen [2]: the output T that is, the product of the mean pressure and the volume taken out per second under a pressure difference of 1 microbar, the volume being measured under the pressure p is constant. Let b be the constant value. If S is the cross-sectional area of the stream, u the drift velocity, and p the mean pressure of the gas along the tube, we have

$$b = \frac{Spu}{p_B - p_A},$$

but

$$p = \frac{p_B + p_A}{2},$$

so that

$$\frac{p_B + p_A}{p_B - p_A} = \frac{2b}{Su}$$

and

$$\frac{p_A}{p_B} = \frac{1 - \dfrac{Su}{2b}}{1 + \dfrac{Su}{2b}}. \qquad . \qquad . \qquad .$$

The ratio of the pressures at A and B is thus independent of the mean pressure. Since the stream velocity of the obviously increases with the speed of the moving boundary it is seen that, in theory, the pressure ratio can be made small as we please. It is also evident that if the velocity of the boundary were even slightly greater than the mean velocity of the molecules, only a very small number of molecules would, after impact, have a velocity component in

[1] M. Knudsen, *Ann. d. Phys.*, **28**, 75-130, 1909; W. Gaede, *ibid.*, 337-80, 1913.

[2] *Vide* the treatment of Knudsen's first paper in *Idées modernes sur constitution de la Matière*. Dunoyer, *Soc. de Phys.*, 1913.

ection BA. But it is not necessary to give the boundary
ch high velocities. Instead, a number of similar systems
placed in series, the high-pressure side of one being
ned to the low-pressure side of the next, and so on. If
re are n systems of this type, the ratio of the extreme

sures will be the nth power of the ratio $\dfrac{p_A}{p_B}$.

constant b depends on the geometrical dimensions
apparatus and on the density of the gas : it is inversely
portional to the molecular weight. The higher the

lecular weight, the smaller the ratio $\dfrac{p_A}{p_B}$ and, therefore,

e smaller the limiting pressure.

Gaede Molecular Pump. Gaede [1] was the first to design a
mp which worked on the principle outlined above. The
mp (fig. 16) consists of a bronze cylinder B, the ends of
ich are closed by two side plates E, which act at the same
ne as bearings for the rotating part A.[2] This is a solid
ass of bronze in which a certain number of circular grooves
ght in the figure) have been cut. The clearance between
e rotating cylinder and the outer case is of the order of
)r mm. This cylinder has a diameter of about 10 cm. The
ooves are divided into two symmetrical groups. The
ir nearest the middle are deepest (23 mm. deep), whilst the
ter grooves are only 13 mm. deep. The gas is most rarefied
the middle, so that it is possible, and advantageous, to have
e biggest cross-section there.

A set of projections, like the teeth of a comb (C in the
ure), fit into the grooves, leaving about 0·1 mm. play
tween the faces of the grooves and the sides and ends of
e teeth. If the cylinder turns in the direction of the arrow,
s accumulates in the m end of the grooves, and the pressure
lowered at the n ends. Owing to the slow rate of diffusion
rarefied gases through narrow openings, very little gas

W. Gaede, *Phys. Zeits.*, 13, 864–70, 1912 ; and *Verh. d. deuts. Phys. Ges.*,
775–87, 1912. *Ann. der Phys.*, pp. 337–80, 1913. See also L. Dunoyer,
letin de la Soc. de Phys., p. 100, 1912 ; and K. Goes, *Phys. Zeits.*, 13,
5, 1913, and 14, 170, 1913.
I am indebted to M. Holweck for fig. 16.

passes from *m* to *n* through the slits left between th
and the sides of the grooves.   In the same way there
circulation between the rotating cylinder and the oute

The gas which accumulates at the *m* end of a groov
an easy outlet through a series of channels *F* which
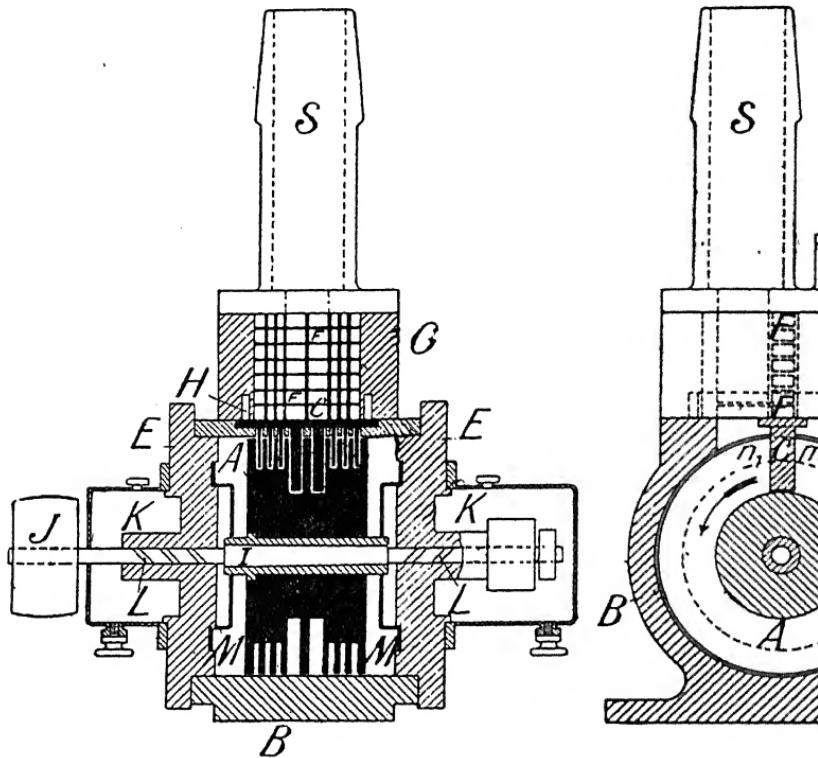
FIG. 16.

into communication with n_2, which is symmetrical w
with regard to the median plane ; similarly m_2 is joi
n_3, which is also symmetrical with n_2 ; then m_3 with *ı*
so to the last *m* space, which is in direct communicatio
the fore vacuum through the tube *T*.   The first *n* s
joined to the vacuum chamber or tube system thro
which is about 30 mm. diameter.   Either a grou
cemented joint is made at *S*.

If the working of the pump is going to be in accordan

tion (2), the fore pump must give a sufficiently low
sure, the limit necessary depending not on the speed of
tion, but on the dimensions of the grooves and of the
h projecting into them.   This is clearly shown in the
e given below.

is not astonishing that the ratio $\dfrac{p_1}{p_2}$ does not even tend

constant value, but seems to pass through a maximum,
ause the limiting pressure at the low - pressure (high
uum) end is never zero because of the vapours present,
se being given out continually by the walls of the tube
stem which is being evacuated.   Thus when the limiting
value of p_1 is reached p_2 can only vary slowly ; and if p_1 is

lowered the ratio $\dfrac{p_1}{p_2}$ decreases.   From this it will be seen

that it is useless to use a fore vacuum pressure less than
10μ, and that quite a low limiting pressure $(0\cdot01\mu)$ can be
got with a fore vacuum pressure of 100μ $(0\cdot1$ mm.$)$.

Revolutions per minute.	Fore vacuum pressure p_1 in μ Hg.	Pressure obtained p_2 in μ Hg.	Ratio $\dfrac{p_1}{p_2}$.
4,000	20,000	3000	6·7
,,	10,000	80	125
,,	1,000	0·3	3,333
,,	100	0·03	3,333
6,000	20,000	800	25
,,	10,000	2	5,000
,,	1,000	0·05	20,000
,,	100	0·01	10,000
8,200	20,000	5	4,000
,,	10,000	0·05	20,000
,,	1,000	0·02	50,000
,,	100	not measured.	
12,000	20,000	0·3	66,000
,,	10,000	0·03	333,000
,,	1,000	0·005	200,000
,,	50	not measured.	

The speed of this pump is remarkable.   Curve A of fig. 13
shows the variation of the speed when evacuating a capacity

of 8 litres through a large bore tap opened for 10 seconds; the pressures p and p', before and after this interval, were measured with a McLeod gauge. The output S'' is calculated from Gaede's formula with relation to the mean pressure $\dfrac{(p+p')}{2}$. The abscissæ are the values of $1+\log\dfrac{2}{p+p'}$. The dotted curve is for a cemented joint between pump and receiver; the full line is for a ground joint with tap grease. The maximum output reaches 1400 c.c. per sec. at a pressure 10μ.

Before leaving this description it is important to notice the way in which both the lubrication and gas tightness the bearings, through which the axle I passes, is assured The axle is turned by a belt passing over a pulley J. The oil from two cups K fills a spiral channel L bored in the axle. The atmospheric pressure tends to force the oil into the pump, whilst the centrifugal force tends to expel it, so that an equilibrium state is reached. This arrangement makes it necessary to start the molecular pump before the fore pump; otherwise oil gets in quickly. The oil always gets in slowly, and the diaphragms M have been put in to stop it, the clear-ance between the diaphragms and the axle being small. precaution is not sufficient, and in the end the oil guar up and a little oil flows down into the bottom of the cylinc opposite the grooves D. When this happens the pump working and the whole thing must be taken down and cl with ether. To get rid of this trouble the makers have the tap leading to the fore pump in such a way that th cannot be opened until the rheostat handle for the mole pump is running at full speed. The arrangement prevents the pump from being stopped before the pre inside it is again atmospheric.

The Holweck Molecular Pump. This pump works on same principle as Gaede's molecular pump, but it embo some improvements on the latter. The whole of the revol part is in the fore vacuum, without any connection thr the axle to the outside, and from a mechanical point of the pump is much simpler than the Gaede. The revol part is a smooth cylinder; the fixed case has no comb arra

; and the joining up of the channels along which the
;ules are sent, by successive impacts on the revolving
ler, is managed very simply by making the channels
ϑ form of a spiral groove cut in the walls of the fixed
ler.   The arranging of the whole of the revolving part
e fore vacuum gets rid of the inevitable leaks which
in the outer casing of the Gaede, and also the troubles
o oil leakage into the pump.   The suppression of the
allows the clearance between the moving and fixed
lers to be reduced to 0·03 mm. at most.   It is through
learance that molecules can get back from one groove
e next groove on the lower pressure side, and in the
Gaede, the clearance of 0·1 mm. between the teeth of the
;omb and the revolving grooves lets the molecules back much
more easily than in the Holweck.   Thus the limiting pressure
in the latter should be at most equal to that of the Gaede.
Moreover, the output is easily made bigger than that of the
Gaede because the diameter of the revolving cylinder can be
made larger, and the section of the grooves can also be
increased.

Fig. 17 is a section of the pump by a diametral plane.
The outer case C is a bronze cylinder on the inner surface of
which the two spirals G, in opposite senses, are cut out.   The
ends of the spirals M run into the end of a radial tube A,
which is the low-pressure end of the pump.   The other ⌐ ⌐
of the spiral grooves come opposite the ends, marked P in
the figure, of a channel joined through B to the fore vacuum.
The depth of the grooves diminishes as they go outwards
from the middle, to allow for the decrease of mean free path
of the molecules with increasing pressure.   The rotating
cylinder D consists of a bronze (or duralumin) tube with a
polished surface.   Into the ends of D are fitted the solid
side plates of the axle E.   The axle works in ball-bearings F,
and one of its ends carries the rotor of a small rotating field
motor. J is the stator of the motor.   A very thin metal
casing K comes in between the pole pieces.   It is made thin
to cut down eddy current losses.   The inside of K is joined
to the fore vacuum through the holes O.   The bearings should
be lubricated with a trace of vaseline when the pump is

assembled. If it is run continuously, this should be renewed
every three months. The vapour from the grease will
obviously cause no interference with the fore vacuum pressure,
which is got with an oil pump. There is no pressure difference
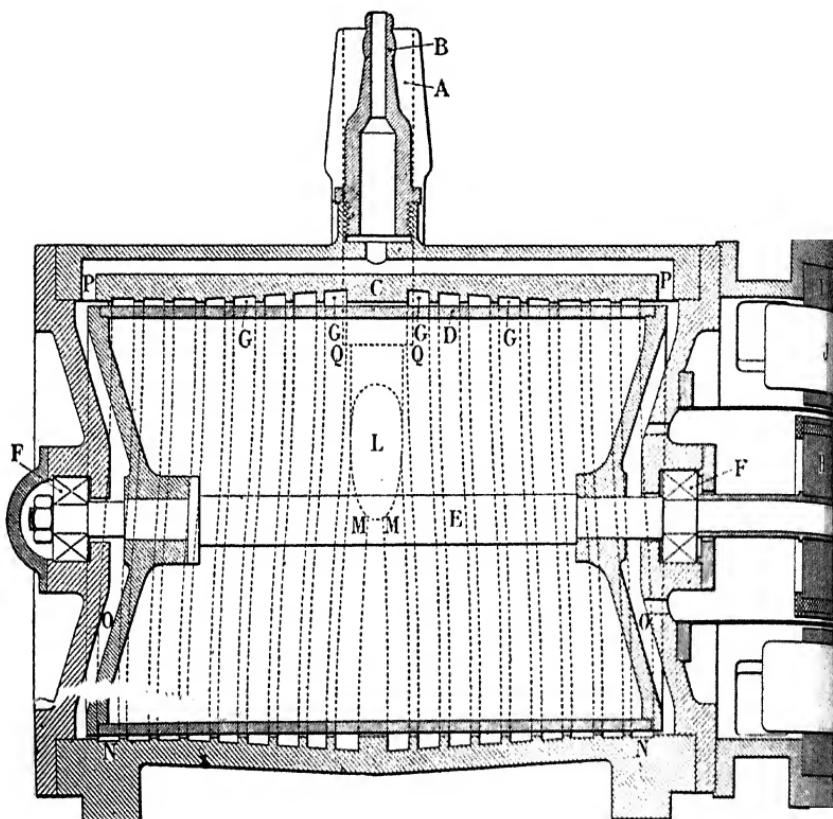
FIG. 17.—Model No. 2, May 1922.

A, low-pressure end of pump ; B, high-pressure end leading to fore pump ; C, pump body, of brass;
D, drum of duralumin ; E, axle ; F, F, ball-bearings ; G, G, spiral channels, left- and right-
handed, decreasing in depth ; H, rotor of the driving motor ; I, stator of motor ; J, field coils
of stator ; K, gas-tight hood, of constantan, enclosing the rotor in the fore vacuum ; L, opening
of intake tube ; M, M, ends of the grooves ; N, N, other ends of the grooves coming out into the
spaces O, joined to the fore vacuum through the channels P ; Q, Q, seating of wire gauze.
The distance between the drum and the pump body and the depth of the N ends of the grooves
are exaggerated.

tending to remove the grease from the bearings, and the
lubricant causes none of the troubles met with in the Gaede
due to the oil.

The motor only takes about 10 watts for 4000 revolutions
per minute when the vacuum is established.

valls and the jet is drawn along with the jet, so that the air
pressure increases in the direction of the stream. Leblanc
also showed that, o. are results got with one of these pumps
withdrawn into 7 cylinder about 15 cm. in diameter, and 22 c...
7 turns to each spiral, working at 4000 revolutions
per minute, with a fore vacuum pressure of about 1 mm. Hg.
The pump lowered the pressure in a 5-litre vessel from 0·1 mm.
to 0·001 mm. in 10 seconds. The mean output according to
Gaede's definition is 2300 c.c. per sec. The mean output of
a Gaede under the same conditions is 1100 c.c. per sec.

It is obviously possible to increase the output, for the same
speed of rotation, by making the grooves deeper, and thus
decreasing the resistance to the flow of the gas. The author
found recently that, by increasing the depth of the grooves, at
the middle, from 7 to 12 mm., the output was nearly doubled.

The limiting pressure depends, for a given number of revolu-
tions per minute, and given fore vacuum pressure and state of
surfaces, on the clearance between the rotating cylinder and
the fixed casing. As has been mentioned above, this is about
0·03 mm. The importance of the fineness of this clearance is
easily noticed if the cylinder is mounted slightly eccentrically,
in which case the limiting pressure rises. The following
results were obtained by Holweck with two pumps of this type
(the best and the worst of a batch), both at 4500 revolutions
per minute. In the better pump (first pump in the table),
the clearance between rotating cylinder and fixed case was
0·025 mm., and for the other (second pump in the table), the
clearance was 0·05 mm.

Minimum pressure obtained p_2.	First pump.		Second pump.	
	Fore vacuum pressure p_1.	Ratio $\frac{p_1}{p_2}$.	Fore vacuum pressure p_1.	Ratio $\frac{p_1}{p_2}$.
μ.	mm.		mm.	
<0·001	0·01–70	70.10^6	0·01–20	20.10^6
0·004	,,	,,	25	6.10^6
0·008	75	9.10^6	30	4.10^6
0·016	80	5.10^6	35	2.10^6
0·048	88	1·8.10^6	38	0·8.10^6
0·330	90	0·27.10^6	40	0·12.10^6

assembled. If it is run continuously, this should be renewed
every three months. The vapour from the grease will
obviously cause no interference the Holt a fore vacuum pressure,
in the ... it is seen that with the Hol a fore vacuum pressure,
unnecessary to use a low fore vacuum pressure (pressure difference
is always an advantage), because the limiting pre.
lower than 0·001μ even when the fore vacuum pressure is
20 mm. Hg. or more. For a fore pump one of the small-
toothed wheel pumps already described would do quite well.
This possibility of high fore vacuum pressure is due to the
:act that the ratio between the fore vacuum pressure and
the limiting pressure is much greater for the Holweck pump
than for the Gaede (of the order of 10^7 against 10^5). The
difference is due to the smaller clearance, as described above,
and also to the greater cross-section of flow and the greater
linear velocity for the same angular velocity. This is shown
by equation (2), putting the output b constant in order to
compare the two types. The table given above shows that
the pump starts to work as a molecular pump when the fore
vacuum pressure falls below a definite limit. The measure-
ments were made with a Knudsen absolute manometer, which
measures the total pressure of the residual gases and vapours.

It must be remembered that, in order to get the best out
of a molecular pump, there must be no traces of slowly
vaporising substances, like grease or mercury, on the surfaces
of the cylinder or case—above all, in the middle parts. A very
small quantity of mercury introduced into the pump will
completely ruin it, if it amalgamates the surfaces. When this
happens the limiting pressure rises to the saturation pressure
of mercury vapour, at ordinary temperatures about 1μ. In
order to avoid this Holweck proposes to make pumps entirely
of steel.

C. Mercury Vapour Pumps. *Preliminary Remarks.* More
than ten years ago Maurice Leblanc showed that it is possible
to get a vacuum of the order of 1 mm. of mercury in the con-
denser of a steam engine by using a steam injector. If we have
a pipe *a* (fig. 18), which penetrates a canal of the form
appropriately called a diffuser, and a jet of steam under fairly
high pressure is forced from the pipe, it is possible to design
the shapes of the orifice and diffuser in such a way that the
walls of the latter are always close to the jet without actually
touching the fluid. Owing to viscosity the air between the

alls and the jet is drawn along with the jet, so that the air
ressure increases in the direction of the stream.   Leblanc
lso showed that, once the action started, the jet could be
withdrawn into the position shown in fig. 19, without any of
the vapour sticking to the walls of the diffuser.   The output
is then greatly increased, since the air is then dragged in
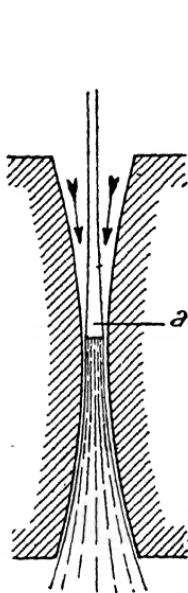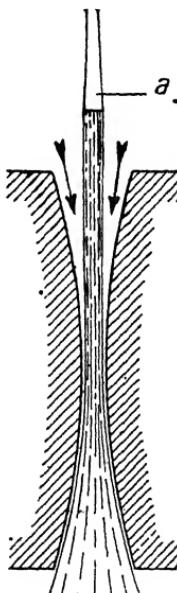
FIG. 18.   FIG. 19.

round the free jet instead of through the small annular space
between the jet and the diffuser.

The water-jet pump (filter pump), which is very useful in
the laboratory, since it gets down to from 20 to 15 mm. if
the water pressure is regular and sufficiently high, works in
a very similar way to the steam jet.   The liquid jet, which is
forced out of the conical nozzle (a in fig. 20), drags along with
it the air which surrounds it, and this forms a sheath round
the jet when it enters the bell-shaped opening b.   When the
sheath becomes thin enough the air emulsifies with the water
in the jet and the bubbles of air are carried along with the
water.   The pump will not work unless this air sheath is
formed at the top of the bell-shaped tube : and the higher

the water pressure the longer the sheath, and the better the pump works. When the water pressure is too low to form a sheath, the water sticks to the sides at the opening of b and the pump will not work.

The above remarks are included here in order to emphasise the fact that the action of the mercury vapour pump is quite different from that of the jet considered above. In mercury
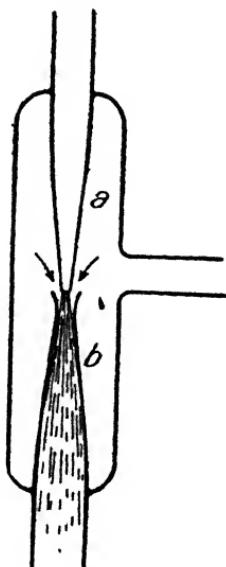
FIG. 20.

vapour pumps the size of the orifice through which the vapour is driven is only of secondary importance. The viscosity of the gas plays no part in the action. The phenomenon occurring in these pumps is the diffusion of the gas into the vapour. The lower the pressure the better the diffusion, since the mean free path of the molecules increases as the pressure decreases. These pumps can be called molecular pumps because their working depends on the motion of individual molecules of the gas. Thus they work at very much lower pressures than those at which the gas can be drawn along by viscous forces.

Consider a tube along which a gas is flowing in the direction indicated by the arrow in fig. 21. Let us call the moving gas the gas G. C is a porous plug in the side tube D. A certain

amount of the gas G will diffuse through the plug and get into D ; but at the same time the gas originally in D, which we shall call the gas E, will diffuse through the plug and mix with the stream in AB and be drawn along with the stream. After some time the tube D, and all the tubes connected with it, will be filled with the gas G, whilst the amount of the gas E in these tubes will continually diminish.

Now if the gas G is a vapour which is condensed in D, the action will still take place. The concentration of the gas E in D will continually diminish, whilst increasing amounts of
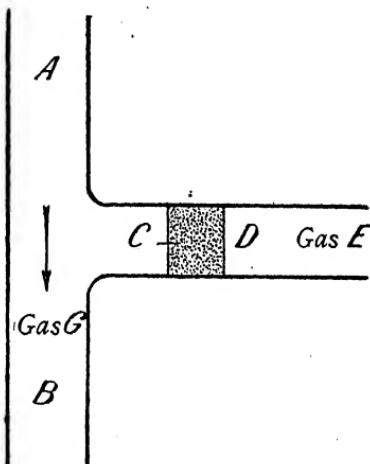
FIG. 21.

liquid produced by condensing the vapour G will accumulate in D. If the liquid has only a small saturation pressure at the temperature established in D, then the pressure there will continually diminish. This is the principle which was used first by Gaede [1] in the mercury vapour pump which he called a " diffusion " pump.

It will be seen that a " diffusion " pump must at the same time be a " condensation " pump, although Langmuir has tried to separate pumps of this type into two separate types. It is true that Gaede does not seem to have realised that, by properly directing the vapour current and making it condense under certain conditions, it is possible to make diffusion easier.

[1] W. Gaede, *Ann. d. Phys.*, pp. 357–92, 1915.

It is clear that, from considerations of how diffusion takes place, the porous plug is not essential.   If the side tube D is cooled rapidly enough, so that all the vapour passing into it is condensed, the gas will diffuse directly into the vapour before it is condensed, and if the tube D be bent downwards
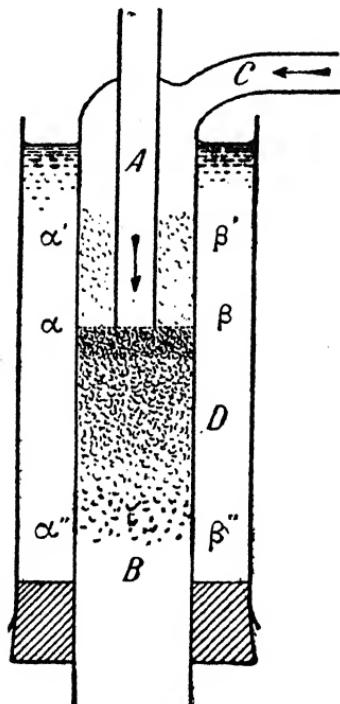
Fig. 22.

the condensed liquid can run into DB, so that there is no accumulation of liquid in the tubes requiring evacuation.

It is true that the gas will diffuse into C, where the vapour is moving in the opposite direction to the gas, and so slows down the diffusion.   This drawback is easily surmounted, as shown in fig. 22.   The tube A, along which the vapour flows, opens into a much wider tube B, which is joined through C to the vacuum apparatus. B is cooled by means of a jacket D. If this were all, the vapour would now condense throughout the annular space between a plane $\alpha'\beta'$, above the orifice, and a plane $\alpha''\beta''$ below it ; since the molecules of vapour coming

from the orifice are moving in all directions. Thus the diffusing gas would still meet a stream moving in the opposite direction to the direction of diffusion.

But if the pressure in B is diminished by a fore pump until the mean free path of the molecules is equal to or greater than the annular distance between A and B, this will no longer take place. Let us consider the molecules inside the orifice and in the plane $\alpha\beta$. Only those molecules with a downward component will leave the tube A. If the total pressure in B is high, these molecules will collide many times with other molecules before reaching the walls of B and condensing there ; so that a large number of vapour molecules will get above the plane $\alpha\beta$. But if the pressure in B is sufficiently low, so that most of the molecules at the orifice with a downward component will strike the walls of B without colliding with other molecules, the vapour will not rise above the orifice. In this case the diffusing gas will not encounter a contrary stream of vapour.

The above argument takes for granted that condensation takes place as soon as the vapour molecules strike the cooled surface, without any such molecules rebounding. Knudsen [1] has shown that this will only happen if the temperature of the cooled surface is below a certain critical temperature, which, in the case of mercury, is well below 0° C. This could be arranged for without difficulty, but in practice it is unnecessary. Diffusion will always take place. The above arrangements tend only to increase the speed of diffusion. Experiment shows that, if the fore vacuum pressure is low enough, the condensation of vapour above the plane $\alpha\beta$ is small enough to allow the pump to have quite a big output. The fore vacuum pressure required depends on the diameters of the tubes A and B : the mean free path of gaseous molecules at atmospheric pressure being of the order of 10^{-5} cm., it will be of the order of 1 cm. at a pressure 10^{-5} bars, that is, 10 microbars, or about $0\cdot01$ mm. of mercury. With this fore vacuum pressure the distance between A and B could be about 1 cm.

If the vapour were all condensed, the limiting pressure

[1] M. Knudsen, *Ann. d. Phys.*, 50, 472–88, 1916.

obtainable would be zero, since there is no limit to diffusion. The speed of a pump of this type is theoretically constant once the pressure in C becomes so low that its flow is independent of viscosity, and obeys the law discovered by Knudsen. According to this law the volume of gas removed, measured at the mean pressure of the stream, is also independent of this pressure and proportional to the cube of the diameter of the tube along which the gas is flowing, and inversely proportional to its length. Gaede [1] has shown that if a gas diffuses into another gas or vapour in a tube of diameter D and length L, under a pressure so low that the mean free path is equal to or greater than D, the volume of gas diffusing per second across a right section of the tube, this volume being measured under the mean pressure of the gas, is independent of this pressure and is given by the formula

$$V = k\pi \frac{D^3}{L},$$

in which k is a constant depending on the nature of the two gases. The rate of diffusion is identical with the speed S' of the pump, defined in paragraph 2. Theoretically a diffusion and condensation pump has a constant speed and a low limiting pressure zero.

Gaede's " Diffusion " Pump. Gaede designed a pump in which diffusion of the gas took place across a slit which had a width approximately equal to the mean free path of the molecules under the pressure existing at the slit. From the reasoning given above it is seen that this adjustment of slit width was useless. The pump is interesting historically, since it was the first diffusion and condensation pump, but it was never much used, because Langmuir showed, soon after the publication of Gaede's paper, that a much simpler arrangement gave very much better results.

V (fig. 23) joins on to the fore vacuum pump. The mercury in A is heated and the vapour rises through B and drops through the tube D, which is constricted at its lower end. The vapour condenses in E, which is surrounded by the cooling jacket K_3K_4, and the mercury flows back into A.

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[1] W. Gaede, *Ann. d. Phys.*, 46, 357–92, 1915.

The steel hood C, which sends the vapour rising through –
into D, has a slit S. The width of the slit can be varied by
the screws H. The diffusion of gas into vapour takes place
at the slit, the gas coming through F from the apparatus
requiring evacuation. The mercury vapour condensed by the
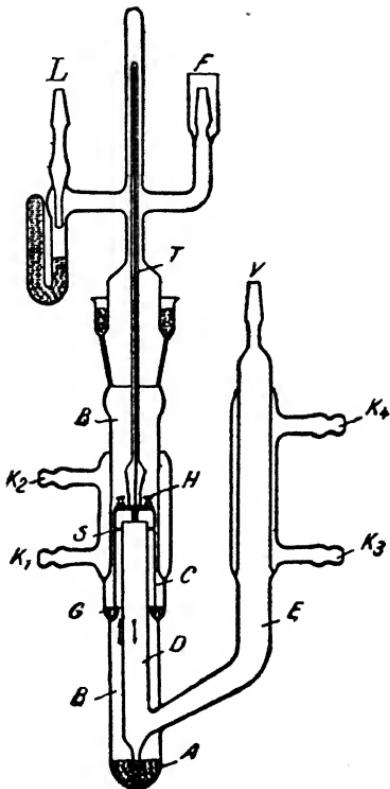
FIG. 23.

jacket K_1K_2 falls into the hollow at G and forms a mercury
seal for the hood C. When the trough is full the mercury
falls back into A. T is a thermometer for finding the effect
of the temperature of the mercury vapour at the level of the
slit. L is a connection with the fore vacuum, so that the
starting of the pump may be quickened when a narrow slit
is used. L is cut out by the shortened manometer when the
fore vacuum is established.

ob⁷Fig. 24 shows the speed of the pump plotted against the
pressure of the mercury vapour, the latter being got from the
thermometer reading. The width of the slit was o·012 cm.
The maximum speed of the pump, 8o c.c. per sec., is got when
the vapour pressure is o·27 mm. (thermometer reading 99° C.) ;
according to Gaede the mean free path of the air molecules
in the mercury vapour is then o·023 : that is, about twice the
width of the slit. The existence of a maximum is to be
expected ; if the pressure of the mercury vapour is too small
the stream carrying the diffused gas will not be strong enough ;
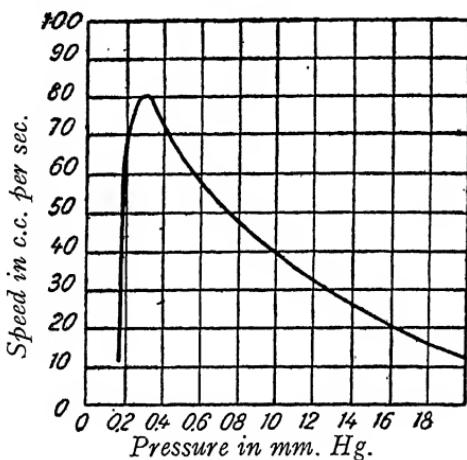
FIG. 24.

if this pressure is too great the flow across the slit will create
a contrary current which will hinder diffusion.

The table on p. 49 shows that the speed of a diffusion
pump is independent of the pressure when the pressure is
low enough. The table also shows that the width of the slit
is not important. The temperature t is the temperature at
the level of the slit.

It will be seen from Gaede's measurements that the speed
of these pumps is fairly low ; it is far less than that of Gaede's
molecular pump, and slightly less than the maximum speed
of the rotary mercury pump (120 c.c. per sec.). But its great
theoretical advantage over other types is that its speed
remains constant well below a thousandth of a millimetre
of mercury.

Width of slit 0·025 cm. $t=106°$.		Width 0·004 cm. $t=110°$.	
·essure p.	Speed S'.	Pressure p.	Speed S'.
μ.	cm.³/sec.	μ.	cm.³/sec.
25	77	70	52
9	72	28	48
2·5	67	6	40
0·8	72	1·5	38
0·2	73	0·4	41
0·06	70	0·07	40

ingmuir's " Condensation " Pump. Fig. 25 shows Lang-
r's [1] first model. The vapour rising from the heated
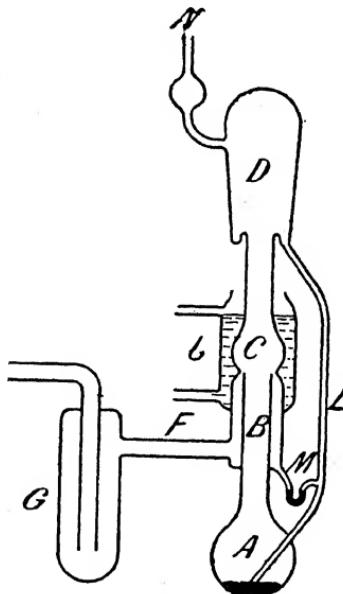
FIG. 25.

rcury in the bulb A rises through B and C into the con-
iser D. The annular space round B is joined to the

I. Langmuir, *Phys. Rev.*, 8, 48–51, July 1916. An interesting note on
history of mercury vapour pumps will be found in this paper. The

apparatus requiring evacuation through F, and the mercury trap G, which is surrounded by liquid air. The tube C widens out just above the end of B and then leads into D, the condenser, from which the mercury flows back into A through L.

A water-jacket J cools the vapour at the end of B; the condensed mercury gets back into A through the trap M. N is the fore vacuum connection.

The following results were obtained by the author with this pump. The fore pump had a speed of 200 c.c. per sec. at 400 microbars, 60 c.c. per sec. at 40 microbars, and zero at 10 microbars.

Times.	Pressure in microbars.		Speed S' in c.c. per sec.
	In D.	In R.	
o	1160	1470	590 cm.^{3}/sec.
30 sec.	720	294	
60 ,,	218	12·8	1150 ,,
80 ,,	18	0·015	3700 ,,

A large number of experiments with hydrogen gave a maximum speed of 7000 c.c. per sec.

This first model still shows a desire to get some kind of slit arrangement, as in Gaede's model. Langmuir and Dushman soon realised that such an arrangement is absolutely unnecessary. Fig. 26, taken from Dushman's articles,[1] gives the details of a glass pump, which is all the more interesting because anyone with a fair knowledge of glass work can make one himself. The proportions of the diagram are incorrect, however. For A a little flat-bottomed flask of 200 to 300

first description of a slitless diffusion pump was given by H. B. Williams (*Amer. Phys. Soc.*, 26th Feb. 1916, and *Phys. Rev.*, 7, 583, 1916). Williams at first proposed varying the width of the slit. The first description of the pump described above was given by H. Hosner, *Gen. Elec. Rev.*, 19, 316, 1916.

[1] S. Dushman, *Gen. Elec. Rev.*, 23, 672–83, Aug. 1920.

c.c. capacity will do. The neck is pulled out and bent over at B, so that the total height of the pump is two or three times the height of the condenser jacket. The orifice L can have any shape whatever. It is easiest to make it straight. Its diameter is unimportant, and can be from 5 mm. to 35 mm. ;
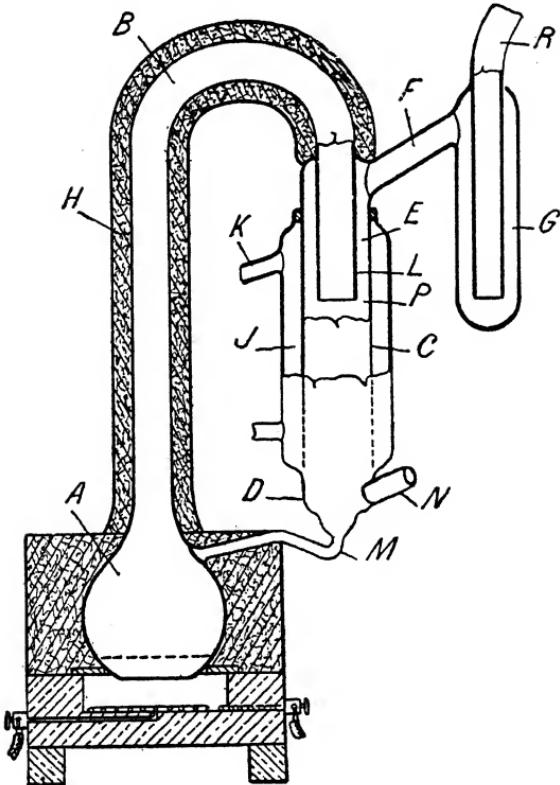
FIG. 26.

however, the amount of heat required will depend on the diameter of L, and the output increases with this dimension. The annular space between L and C, to which the tube L is fused by an inserted joint, should be from 2 or 3 mm. for small diameters of L to 12 mm. for the largest. The only important point is that the level of the orifice should be below the level of the water in the condenser jacket, so that condensation should be as rapid as possible. This cuts down

the contrary current against the gas, which comes in through
F. The pump will still work even if the latter precaution
is not taken, as has been shown both in theory and practice ;
but when condensation takes place at some distance from the
orifice the rate of diffusion and consequently the speed of the
pump are greatly diminished. It is best to have the orifice
about one-third of the way along the condenser jacket, of
which the length should be six or eight times the diameter of
C. The mercury gets back through M, which acts as a cut-
off between the vapour in A and the condensing tube. N is
the connection to the fore pump. The figure shows electric
heating, but a gas burner under A will do quite well. On
account of the temperature differences throughout the pump
it should be made of Pyrex. The trap G stops mercury
vapour from getting into the exhausted apparatus. The
pressure of the vapour will be that corresponding to the
temperature of the walls of the condenser.

The output varies with the diameter of the orifice ; it is
of the order of from 400 to 1500 c.c. per sec ; but it varies
relatively slowly with the rate of vaporisation. The heat
expended can be varied from 220 watts to 550 watts without
changing the output of the pump. The speed of vaporisa-
tion does, however, influence the fore vacuum pressure
necessary for maximum output (although this is theoretically
constant). It is found that with an orifice diameter 22 mm.
the pump works well with an energy input of 220 watts
and a fore vacuum pressure 35μ ; if the energy input is in-
creased to 550 watts, the pump works quite as well from a
fore vacuum pressure 600μ.

This pump can also be made in metal. The disadvantages
of metal are that it necessitates a ground joint or a waxed
joint to the tube system, and that cleaning is more difficult.
The liquid air trap would, of course, take out the vapours
coming from the grease or wax at the joint.

Fig. 27, also from Dushman's articles (*loc. cit.*), shows an all-
metal model in steel ; the diagram seems out of proportion,
being too wide for the height. The mercury is placed in A over
an electric heater. The vapour rises through B, which should
be from 3 to 4 cm. wide and at least 20 cm. long. The

vapour is turned downwards by the hood C, which is supported on short thin rods so that the heat will not get to the joint F. D is the orifice where diffusion takes place, the gas coming from F through the annular space E. J and K are for the water-jacket of the condenser.
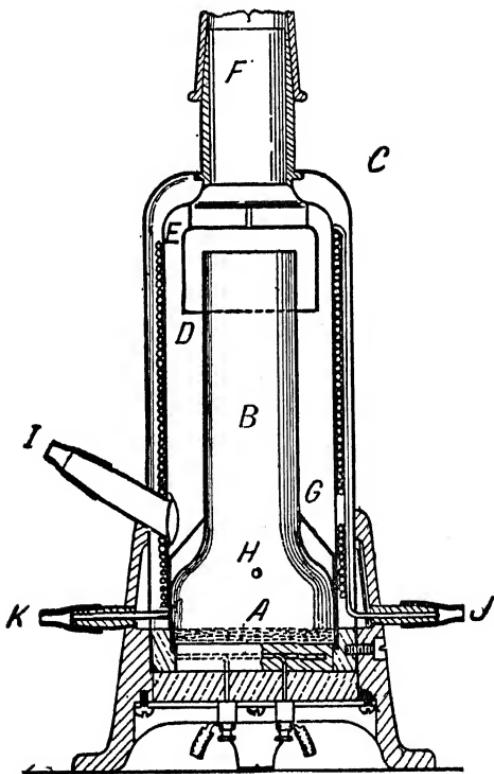
FIG. 27.

All-metal pumps of slightly different design are made by the firm Gaiffe-Gallot and Pilon. The mercury vapour rises along the tube A (fig. 28), in the annular space between A and D. D is double-walled, with water circulation through the jacket, and its lower opening is protected against penetration of mercury vapour by the action of the spherical caps H and K, and by the trough I, which is open at the bottom. The inner wall of D passes through the cover E and has an annular

trough F at the upper end. The trough is filled with vacuum wax to join on to the tube system. Diffusion takes place
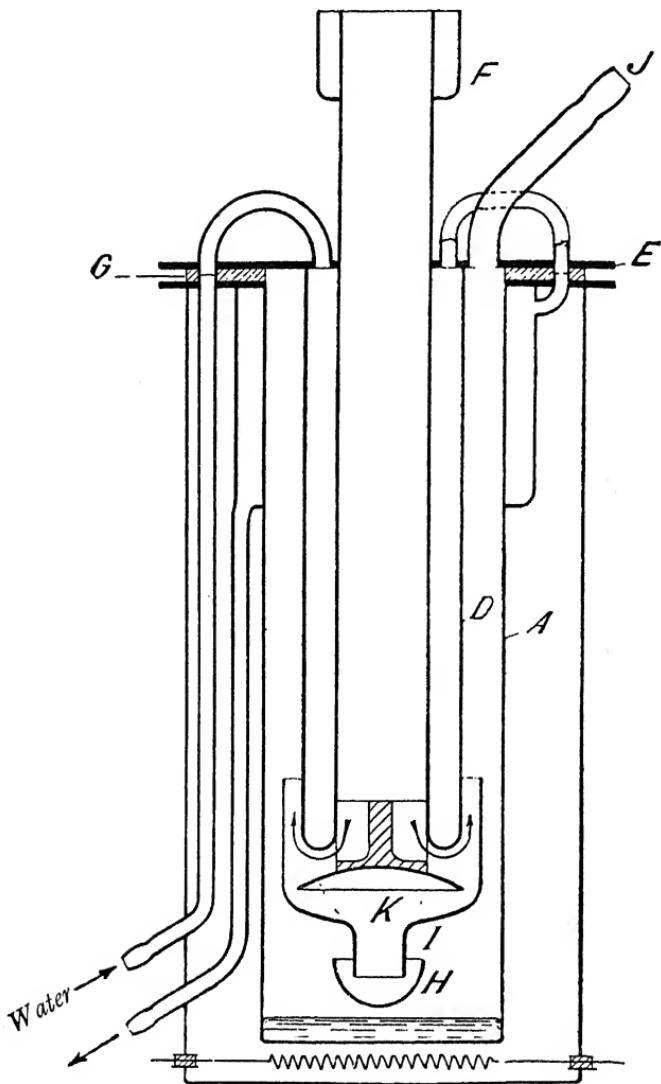
FIG. 28.

between the edge of I and the outer walls of D; condensation takes place on the outer walls of D and the inner walls of A. " The dimensions of the cap and its situation with regard to

: outer condenser and the lower end of the central tube
ve been arranged so that mercury vapour cannot get into
' *J* is the fore pump connection.   The cover *E* is screwed
wn on the rim at the top of *A* with rubber rings *G* between
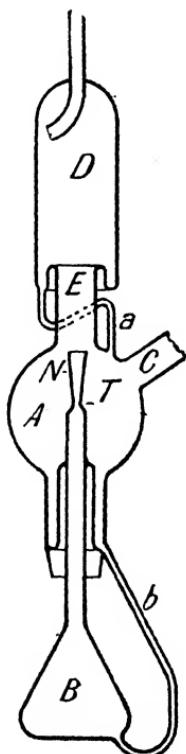
FIG. 29.

:he two.   This makes it easy to take the pump to pieces.
The figure shows the arrangement for water cooling.
   On account of the ease with which mercury vapour pumps
:an be made in the laboratory a great number of different
designs have been constructed.   Six or seven different kinds
will be found in the *Physical Review* for the years 1916, 1917,
and 1918.   Only that due to Crawford [1] will be described here.
Fig. 29 shows the design.   It is peculiar from the fact that the
orifice from which the vapour comes is not inside the condenser,

[1] W. W. Crawford, *Phys. Rev.*, 10, 557, 1917.

which in this case is a bulb D ; and also because the nozzle T is so shaped that it will give a cylindrical jet ; at least, this appears to be so from comparison with the nozzles used by Leblanc. This form of jet has also been used by Stimson [1] in a double pump consisting of two condensation pumps in series. The high-pressure end of one pump is joined to the low-pressure end of the other, the high-pressure end of this being joined to a filter pump which gets down low enough for this type of pump. Fig. 30 shows a double pump of this type, with one heating bulb serving both pumps. The difference between the low-pressure and high-pressure orifices is very marked. It seems that the action at the high-pressure jet, where the pressure is that established by the water pump, is very similar to that in steam jet ; the latter, however, works generally under pressure differences of the order of the atmospheric pressure or more, whilst the mercury vapour jet can only give a pressure which is a few millimetres more than the fore pressure of the water pump. It is probably in this direction that improvements will be made.

The method of heating might also be improved. If these pumps are to work steadily, boiling with bumping must be avoided ; obviously the best way is to heat the surface from which evaporation takes place. Experiments have been made in which a mercury arc is produced, and it has been found that in this case the vapour comes off more freely and with greater velocities. The author has himself obtained some results with this arrangement.

The author has recently made a pump in which the condensation takes place in two stages. In this model, as in that of Stimson, the first mercury jet A (fig. 30A) acts like the steam injector, and is forced into a conical diffuser which is connected to a filter pump as fore pump. This first jet lowers the pressure in B, into which an annular stream of vapour is sent from the sleeve C. This jet still further diminishes the pressure in D, which is joined to the tube system requiring evacuation. The annular jet is formed by vapour which gets into C by the small holes T, the remainder of the vapour going on to form the jet at A. This pump is more compact

[1] H. F. Stimson, *Jour. Washington Acad. Sci.*, 7, 477, 1917.

Heat Insulation

Chamber to be

evacuated
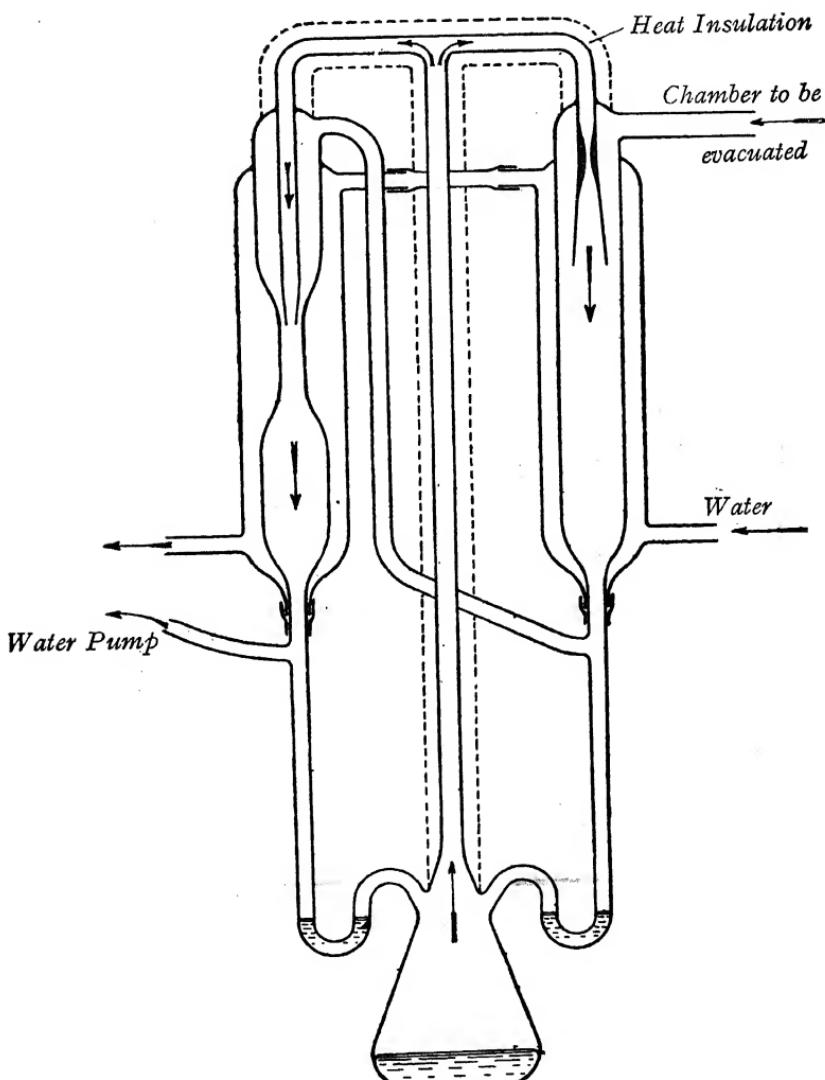
Water

Water Pump

FIG. 30.

than Stimson's, although it is less fragile and easier to mount. The mercury vapour is used nearer the heater, there is less harmful condensation, and the speed is probably greater. For the fore vacuum even a moderately good water pump will do, since it will work from a fore vacuum pressure of 25 or 30 mm. of mercury.
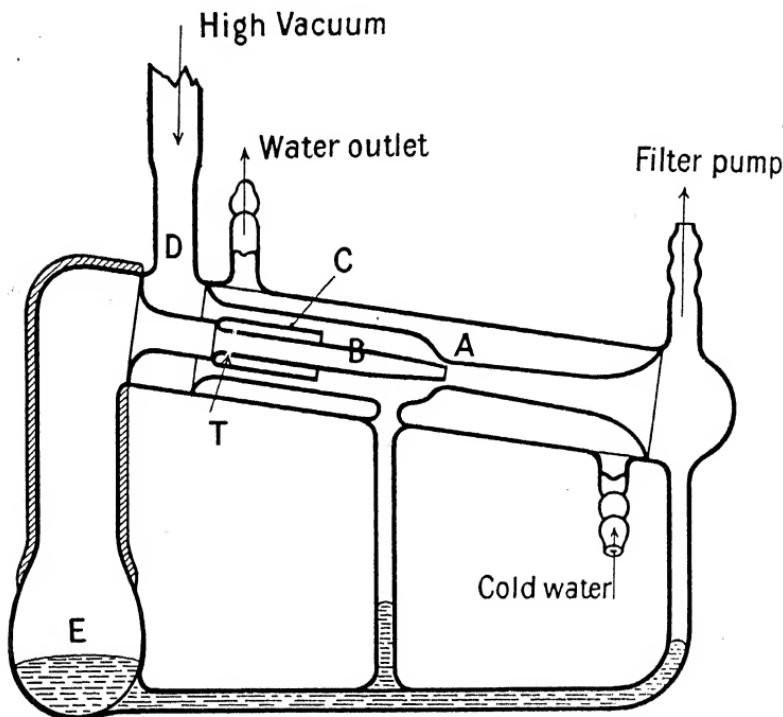
Two Stage Condensation Pump.

Fig. 30A.

Speed and Limiting Pressure of Condensation Pumps. The speed of a glass pump of the type of fig. 25, as has already been mentioned, varies with the diameter of the orifice. For the sizes usually used it is between 400 and 1500 c.c. per sec. Crawford's pump (fig. 29) is stated by him to have a speed of 1300 c.c. per sec., with quite a small orifice.

Detailed measurements of the output of a metal pump have not been published. According to Dushman (*loc. cit.*),

a pump like that of fig. 27, with mercury container 7 cm. in diameter and orifice 3 cm., working from a fore pressure 7μ, and with energy input 300 watts, has an output of from 3000 to 4000 c.c. per sec.

The following results are also due to Dushman. They show very plainly the effect of the speed of the vapour stream on the limiting pressure. These pressures were measured with an ionisation gauge. The fore vacuum pressure was 1.6μ, and was got with an oil pump.

Watts in heater.	Pressure in microbars.
130	0·27
150	0·07
170	0·04
180	0·023
200	0·003
220	0·007
240	0·0025
280	0·002
300	0·002

The limiting pressure is thus lower than that got with a Gaede molecular pump, but higher than that of the Holweck, in which the pressure ratio is of the order of several millions. The manometers used were not, however, the same : Holweck used a Knudsen absolute gauge and Dushman an ionisation gauge. It is probable that the results obtained with the Knudsen gauge are more trustworthy on account of the greater simplicity of the phenomena involved. No figures are available relating to measurements on the Holweck pump with an ionisation gauge ; but a comparison between the two types of pump has been made by the Mullard Radio Valve Company by testing the vacua obtained in triode valves. It was found that for valves of the same volume, and in order to get the valves down to their best working pressure the condensation pump took between two and three times a long as the Holweck molecular pump.

This result is also interesting as showing the difficulty o

accurate measurement of output at low pressures, and the difficulty also of measuring very low pressures. It is doubtful whether a pressure of 10^{-4} microbars (0.000074μ) has ever been reached, although we have quoted the result above. But it is some satisfaction to realise that at a pressure of 10^{-3} microbars, which has certainly been reached with the Holweck pump, a molecule of air travels on the average 80 metres without meeting another molecule.

CHAPTER II

MANOMETERS

1. **Classification.** A large number of manometers or gauges for measuring low pressures have been designed and tried. Only a few have been found to be of practical value, and these will be described in detail. Short descriptions are given of some of the others, and the bibliography at the end of the book contains further references.

The instruments used in practice for measuring low pressures belong to two different classes. The first class work by comparison of the unknown pressure with a known pressure ; either by the difference of level of liquid columns or by the bending of an elastic diaphragm which separates the gas at known pressure from the gas at the unknown pressure. The second class, of more recent origin, depend on various properties of gases which vary with the pressure, or, more precisely, with the number of molecules per unit volume. The best-known gauges of the second category are Knudsen's absolute gauge, Pirani's gauge working on the thermal conductivity, and the ionisation gauge. The McLeod gauge belongs to the first category, and it has been, and still is, the most used gauge for low-pressure measurements ; but it is not suitable for all purposes. The perfecting of pumps, as described in the first chapter, enables us to reach pressures of $0 \cdot 01 \mu$ and sometimes $0 \cdot 001 \mu$. Therefore it is obvious that if we are going to utilise these low pressures we must not introduce a manometric liquid whose vapour pressure exceeds the limiting pressure of the pumps. But no known liquid has such a low saturation pressure at room-temperature. Mercury, the most convenient liquid for manometers in

spite of its high density, has a saturation pressure of about 1μ at 20° C.

The McLeod gauge can only be used for gases which obey Boyle's Law ; besides which, each reading necessitates an operation which excludes all possibility of instantaneous reading or continuous registration. For continuous registration ordinary connecting tube manometers, or those with elastic membranes, are suitable. Lord Rayleigh [1] made and used a mercury manometer for instantaneous reading. Measurements were made by having a mirror attached to the manometer and finding the angle through which the manometer had to be turned to bring the surfaces into contact with glass points. Shrader and Ryder [2] have recently described a similar manometer which is very suitable for continuous registration. On one of the mercury surfaces is a little glass float which is fixed at the end of an optical lever of which the axis of rotation is fixed to the sides of the tube, the whole of the optical lever being inside the manometer. The limiting sensitivity of these manometers is 1μ. This is also about the limit of the corrugated membrane manometers, [3] which are also suitable for continuous registration.

2. **The McLeod Gauge.** (a) *Principle and Description.* The principle of the McLeod gauge consists in isolating a known volume V of the gas at the unknown pressure x and compressing the gas into a small known volume v, at which the pressure is measured. If h is this pressure, then, according to Boyle's Law,

$$x = h\frac{v}{V}.$$

Thus the gauge depends on the applicability of Boyle's Law. It consists of a bulb B (fig. 31), with a narrow tube C at the top, and joined at A to the vacuum apparatus when the mercury level is at F. The volume V is the volume of the bulb, together with that of C, which is cut off when the

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[1] Lord Rayleigh, *Phil. Trans. R.S.*, **196** A, 205, 1901.

[2] J. E. Shrader and H. M. Ryder, *Phys. Rev.*, **13**, 321, 1919.

[3] Scheel and Heuse, *Zeitschr. f. Instrumentenkunde*, **29**, 14, 1909. The author himself made a manometer of this type in 1906, which gave a deflection of 1 mm. on a scale at 1 metre for a pressure difference of 1μ.

mercury reaches A. v is the volume between the top of C and a graduation on the tube. When the mercury is raised until the level reaches this graduation in C, it will rise to a higher level in D, and if C and D have the same diameter, the difference of level h measures the pressure of the compressed gas so long as the initial pressure is very small compared with h—that is, so long as the ratio $\dfrac{V}{v}$ is large enough. This approximation is evidently valid, since the ratio $\dfrac{V}{v}$ can be made 100 or 1000 or more. The pressure h will then be at least 100 times greater than x. Owing to other causes, the probable error is usually at least 1 per cent.

For raising and lowering the mercury either of the arrangements shown in figs. 31 and 32 will do. In the first, the reservoir G, containing the mercury, is joined to the gauge by a flexible rubber tube, and the level of the mercury is changed by raising or lowering G. In the second arrangement the reservoir G is fused on to the gauge, and it has a small side tube E through which the bulb G can either be exhausted or connected with the atmosphere. Between the reservoir and the gauge there is a tap, or, better still, a steel needle valve with a thread cut on the needle which works in the rubber bung which closes the top of G. When the tap or valve is opened and E opened to the atmosphere, the mercury rises in the gauge. The rising is stopped by closing the tap or valve when the mercury level reaches the graduation on C. The needle valve is better than a tap, because the tap grease dirties the mercury and hardens, so that the whole gauge has to be taken down, which is often inconvenient. Besides which, the needle gauge usually allows for a bigger hole for the mercury to flow through, and makes measurement quicker. The mercury level is lowered by evacuating G through E and opening the tap or valve.

The two arrangements described above have both their own peculiar advantages and disadvantages. The first arrangement makes the operation a little quicker, and with it there is little danger of mercury getting into the tube system. With

the second arrangement, if the tap or valve is not closed in time, *G* will be emptied of mercury and air will rush violently
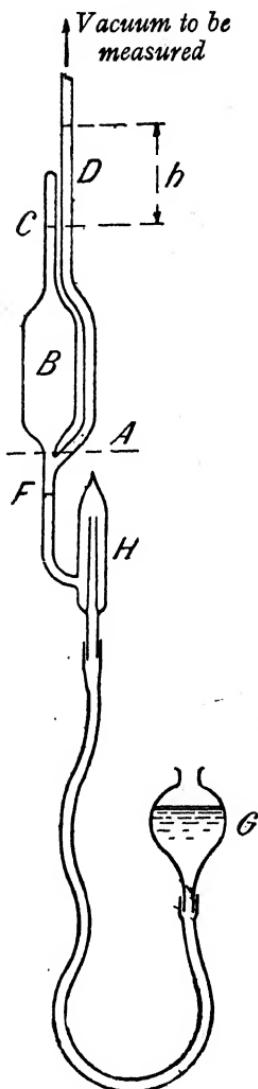
FIG. 31.
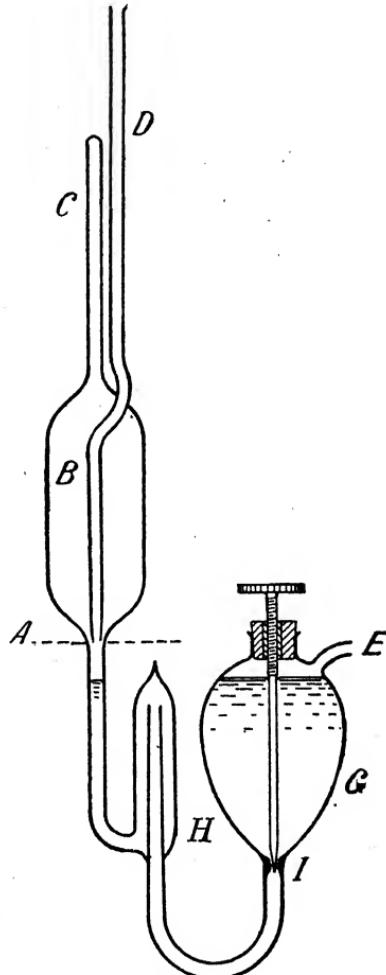
FIG. 32.

through the gauge into the tube system and will probably break something.

In spite of this inconvenience the second arrangement is to

be recommended for gauges used to measure very low pressures, because of the weight of mercury which is then required. If a rubber tube is used, it must, of course, be thoroughly cleaned. This may be done by immersion for twenty-four hours in a boiling solution of caustic soda (dilute), washing it with distilled water and alcohol and drying it by passing a rapid current of air through it to get rid of sulphur dust.

Whatever arrangement is adopted for moving the mercury, it must always pass through an air trap H to get rid of air bubbles which are carried along with the mercury.

The mercury which is used must be very pure. Before it is introduced into the air trap and gauge, these should be evacuated and heated to as high a temperature as possible to get rid of the gas which sticks to the walls.

It will be noticed that the design of the bulb in fig. 32 is slightly different from that of fig. 31. The change has been made with the idea of making the volume V more definite. In the design of fig. 32, V is the volume cut off by the mercury when the level just closes the opening of D. Fig. 33 shows an arrangement like that of fig. 32 but designed for high sensitivity : it will be described later.

(b) *Choice of Dimensions.* At first sight it looks as if the gauge could be made to read any pressure, however small, since it seems to be only a question of making the ratio $\frac{a}{C}$ large enough. But in practice the sensitivity is limited for two reasons. Firstly, if V is greater than 500 c.c. the time of operation becomes very long : Gaede has made gauges with $V = 1000$ c.c., but even with $V = 250$ c.c. the time of operation is a minute at least. Since it is also necessary to allow some time for equalisation of pressure when the pressure is low, this makes it difficult to follow changes of pressure unless they are very slow. As a rule V is rarely made greater than 250 c.c. Secondly, v cannot be reduced indefinitely. The diameter of C should either be constant round the graduation, so that the surface-tension correction is constant, or the part of the tube near the graduation should be calibrated by comparison with a separate tube (E in fig. 33) which has

5

practically the same diameter.   Thus the graduation cannot
be made too near the end of C, because, whatever precautions
may be taken, it is impossible to get a flat end when sealing
with a blowpipe.   In practice it is found that if the diameter
of the compression tube is too small, even if the mercury is
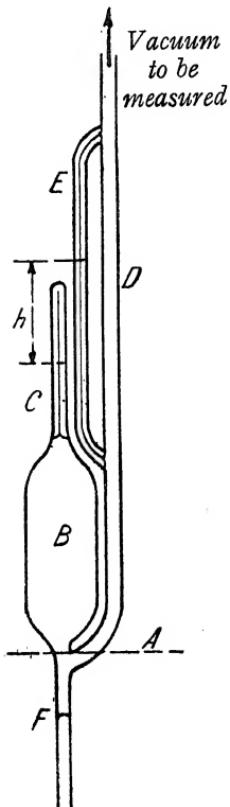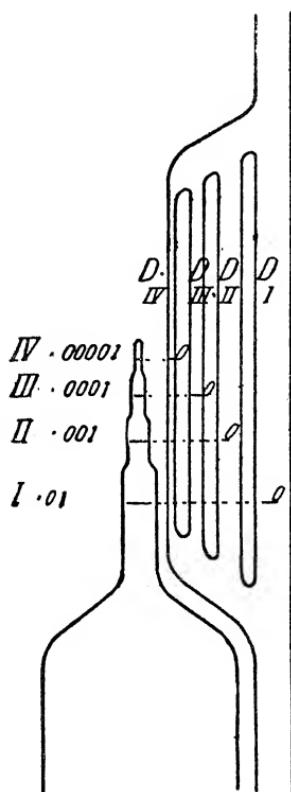
FIG. 33.   FIG. 34.

quite clean, it moves in jerks and it is difficult to get it just
on the mark.   The diameter should not be less than 0·5 mm.,
and even then the slightest trace of impurity on the mercury
surface makes it stick.   Oxygen and some other gases produce
the same effect by contaminating the mercury surface.

If the diameter of C is 0·5 mm., and the distance of the
graduation from the top is 3 mm., the volume v will be 0·6

cu. mm. If V is 250 c.c., then the ratio $\dfrac{V}{v}$ will be 1,400,000, which gives 0.0025μ as the pressure corresponding to a difference of level of 1 mm. This is the practical limit of the sensitivity of the gauge. As a rule the gauge is only useful to measure pressures above 0.01μ, so that the ratio $\dfrac{V}{v}$ can be made about 100,000, which, if $V = 250$ c.c., allows for a 5-mm. compression chamber of diameter 0.8 mm.

If the compression chamber has the same diameter throughout, the range of the gauge is very limited. In practice, with a capillary of 0.8 mm. diameter, the maximum length of the compression chamber is 20 cm. If this is exceeded the gauge is cumbersome and fragile. If the tube E (fig. 33) is 40 cm. long, the gauge will measure pressures between 0.01μ and 160μ (0.4μ for 1 mm. difference of level). It would seem that, *a priori*, too long a capillary would not allow for equalisation of pressure between the bulb and the capillary. However, it will be shown later (Chap. III, § 1) that if the diameter of the capillary is greater than 0.5 mm., the equalisation is very rapid on account of the small volume of the compression chamber.

This limitation of range can be got rid of by using, as a compression chamber, a series of capillaries of decreasing diameter joined together. This is shown in fig. 34. If V is 250 c.c., the following dimensions are suitable :—

Tube I	Graduated for 0.01	Length 50 mm.	Diameter 10 mm.
„ II	„	„ 0.001	„ 20 „	„ 4.5 „
„ III	„	„ 0.0001	„ 20 „	„ 1.5 „
„ IV	„	„ 0.00001	„ 20 „	„ 0.7 „

These sizes are arranged so that the marks will be far enough from the joints, so that the diameters at the marks will not be affected when the joints are made. The greater length of the widest tube will, if the sensitivity is 0.01μ and the length of E is 40 cm., enable the gauge to be used for pressures up to 4 mm., and so reach the lower limit of the ordinary mercury manometer.

The only difficulty of this arrangement is that the surface tension corrections are different for the different marks.

This can be surmounted in two ways. The best way, although it rather complicates the design, is to set up a number of tubes D_1, etc., of equal diameter, parallel to the compression chamber, the second set being joined to the vacuum system. Each tube of this set has a mark which is level with the mark in the corresponding portion of the compression chamber, with the same diameter, and the difference of level can be measured from the mark in the parallel tube. There is thus no need to apply a surface tension correction, and readings are made directly in the various fractions of 1 mm. of mercury. The second arrangement uses a single parallel tube D_1, with diameter equal to that of the widest tube of the compression chamber. The surface tension corrections for the other tubes of the compression chamber are then found by preliminary experiment. This arrangement is not as satisfactory as the first, because the corrections for surface tension are not constant.

(c) *Calibration*. If absolute measurements are required, the gauge must be calibrated. This is done before the gauge itself is joined to the air trap. The upper end of D is joined to a pump (any pump used as a fore pump will do), with a piece of rubber tubing carrying a pinchcock. A tap is fused on to F. The gauge is turned upside down and mercury is let in through the tap until it reaches A, where D is joined to the bulb. Evacuation is necessary in order to get the mercury into the capillary. The air is now let in and the mercury is driven out and weighed. Thus the mass of mercury P which fills V is known, and also the masses $0·00001P$, $0·0001P$, $0·001P$, and $0·01P$, which will fill the different compression chambers. If V is about 250 c.c., the first weight, $0·00001P$, will be about 34 mg. But it is nearly impossible to weigh out a drop of this size with an accuracy of 1 per cent.: even for $0·0001P$ it is difficult. To avoid this, lengths of capillary from which the chambers III and IV were made are taken, and the masses of mercury p_{III} and p_{IV} which fill known lengths l_3 and l_4 are determined. Then a drop of mercury is taken, of which the mass is less than $0·00001P$. The mass is found: let it be P_{IV}. It is introduced into the gauge by means of a drawn-out tube, and the gauge is again

pumped out and the mercury drop is brought into tube IV; the air is let in again, and the drop sticks to the walls of the tube; its level is noted, and the graduation for tube 4 is made at a distance $\dfrac{0 \cdot 00001P - P_{IV}}{P_{IV}} \cdot l_{IV}$ from this level and towards the bulb. The same procedure is used for chamber III. Chambers I and II can be graduated without separate measurement.

There is just one more point worthy of mention concern-
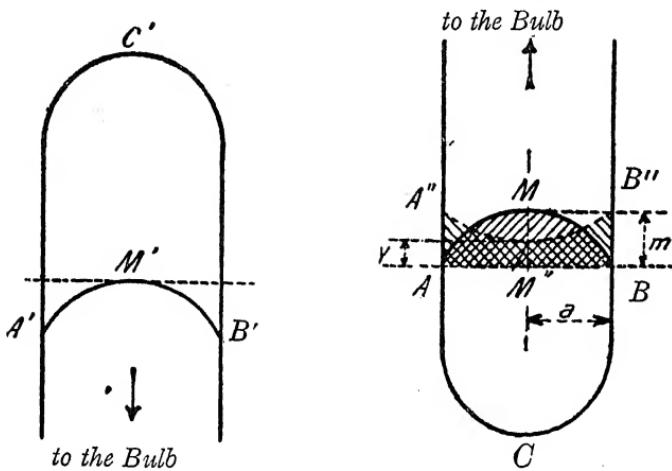
FIG. 35.

ing the calibration. During these operations the gauge is upside down. Suppose that either the simple or compound chamber has been filled with the exact amount of mercury whose volume is the correct volume for one of the compressed amounts v. When the gauge is turned upside down the volume is $AMBC$ (fig. 35). But the graduation ought to be made at M', which is such that when the gauge is turned right side up, the volume $A'M'B'C'$ is equal to $AMBC$. Draw a concave meniscus $A''B''$ such that $A''M''B''C$ is equal in volume to $A'M'B'C'$, and therefore to $AMBC$. The volume of the portion of a sphere cut off at the plane AB must be equal to the volume between this plane and the surface $A''M''B''$: these are indicated by the shading in the diagram. Let m be the height of the meniscus, a the radius

of the tube, and y the distance of the graduation from the plane AB. The relation should be :

$$\tfrac{1}{6}\pi m(3a^3+m^2)=\pi a^2(m+y)-\tfrac{1}{6}\pi m(3a^2+m^2),$$

which gives

$$y=\frac{m^3}{3a^2}.$$

But if ϕ is the angle of contact between mercury and glass, and R the radius of curvature of the meniscus, we have

$$a^2=m(2R-m) \qquad m=R-R\sin\phi,$$

so that

$$a^2+m^2=\frac{2m^2}{1-\sin\phi} \qquad a^2=m^2\frac{1+\sin\phi}{1-\sin\phi},$$

thence

$$y=\tfrac{1}{3}m\frac{1-\sin\phi}{1+\sin\phi} \quad \text{or} \quad y=\tfrac{a}{3}\left(\frac{1-\sin\phi}{1+\sin\phi}\right)^{\tfrac{3}{2}}.$$

The angle of contact varies a good deal, but it is usually about 135°. Therefore

$$y=\frac{m}{3}\frac{\sqrt{2}-1}{\sqrt{2}+1}=0\cdot057m \quad \text{or} \quad 0\cdot023a.$$

Thus the graduation should be just a little nearer the bulb than the base of the meniscus, when the gauge is turned upside down. The above formula gives its exact position when m has been measured. As a rule, the calculation is not worth making. For an error dv caused by an error dl in the position of the graduation is equivalent to an error dh in the difference of level. By Boyle's law

$$\frac{dh}{h}=\frac{dv}{v} \quad \text{so that} \quad \frac{dh}{h}=\frac{dl}{l}$$

if l is the length of the compression chamber. From the error dh we get an error dx in the pressure, which, for any given value of the ratio $\dfrac{v}{V}$, is given by

$$\frac{dx}{x}=\frac{dh}{h}=\frac{dl}{l}.$$

So that, neglecting y, the error in x is given by

$$\frac{dx}{x} = \frac{y}{l} = \frac{m}{3l} \cdot \frac{1-\sin\phi}{1+\sin\phi} = \frac{a}{3l}\left(\frac{1-\sin\phi}{1+\sin\phi}\right)^{\frac{3}{2}} = 0.023\frac{a}{l}.$$

But the radius of the tube is always less than one-fifth of the length of the compression chamber ; therefore

$$\frac{dx}{x} < 0.0046.$$

So that, in practice, when the gauge is reversed the mark should be made at the level of the circle of contact of mercury and glass.

(d) *Conditions under which this Gauge must be used. Accuracy of this Gauge.* The McLeod gauge depends on the validity of Boyle's Law at low pressures, when the pressure ratio used is 10,000 or even 100,000 to 1. It is obvious that this will not apply to easily condensable vapours. Traces of such vapours entirely falsify the results obtained with permanent gases. Results are always bad unless the gas is quite dry. A new gauge which has just been evacuated always gives wrong results, not only because the atmospheric air which remains is not perfectly dry, but also owing to the vapour sticking to the walls of the tubes. The latter not only exerts varying partial pressures, but also affects the surface tension at the mercury glass surface to a different extent at the two surfaces. The following are results got with a gauge of the model given in fig. 33, in which the compression tube has a uniform diameter equal to that of the comparison tube. There were thirty graduations, each corresponding to 1/10,000 of the total volume. The gauge had been carefully washed with nitric acid and distilled water, and dried by a current of air. After pumping for an hour, but without heating the gauge, the following measurements were obtained :—

GAUGE USED FOR FIRST TIME

Compression ratio.	·0030	·0025	·0020	·0015	·0010	·0005	·0004	·0003	·0002	·0001
Apparent pressure,μ	−3·9	−3·9	−1·8	−1·9	−1·2	−·45	−·35	−·06	+·12	+·11

The graduated comparison tube and the compression tube had the same diameter, and the levels in them were the same when they were open to the air. But it is seen that, under the above conditions, except near maximum compression, the mercury level was higher in the compression tube than in the comparison tube, which makes the pressure apparently negative. This was probably due to the fact that drying was quicker in the tube leading straight to the pump than in the compression tube.

After some days' use, connected to an evacuated tube system and to a little phosphorus pentoxide bulb, the same gauge gave the following results :—

SAME GAUGE AFTER DRYING IN VACUO WITH P_2O_5 FOR SOME TIME

Pressure ratio .	·0031	·0025	·0020	·0015	·0010	·0005	·0004	·0003	·0002	·0001
Apparent pressure, μ	6·6	7·5	7·6	7·2	6·6	7·1	7·3	7·1	7·2	7·2

The last five results are the best, and agree very well with one another. They correspond to differences of level from 14·2 mm. to 72·3 mm.

The following results show the effect of the presence of organic vapour in the tube system. The organic substance got in from the pump (a Gaede rotary pump), and scrubbing with *aqua regia* did not entirely remove it from the drum of the pump :—

SAME GAUGE WITH TRACES OF ORGANIC VAPOUR IN THE TUBE SYSTEM

Pressure ratio .	·0030	·0025	·0020	·0015	·0010	·0005	·0004	·0003	·0002	·0001
Apparent pressure, μ	33	11·3	9·2	8·3	7·3	7·3	7·2	7·2	7·1	7·0

Even with gases like carbon dioxide the same kind of error occurs. Lord Rayleigh [1] studied the applicability of Boyle's Law to the " permanent " gases (H_2, N_2, O_2), and found it applied between 1·5 mm. and 0·001 mm. These results were

[1] Lord Rayleigh, *Phil. Trans. R.S.*, 196, 205, 1901.

confirmed by Scheel and Heuse[1] with their membrane manometer. The same workers[2] studied the accuracy of the McLeod gauge for H_2, N_2, O_2, Ne, A, and He; they found that, if the gauge is dry, the results are true down to 0·01 mm. Lastly, Gaede[3] showed that the gauge is quite accurate for
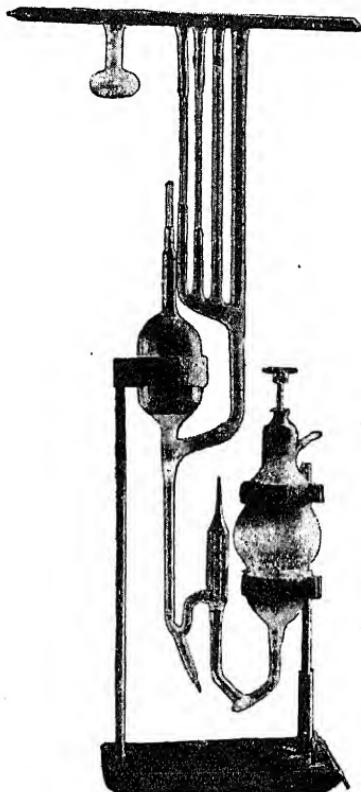
FIG. 36.

H_2 and N_2, even for pressures lower than 0·1μ, so long as the walls are free from moisture and adsorbed gases. The gauge is much less reliable for oxygen owing to the action of this gas on the mercury surface, causing the latter to stick to the glass. The gauge can be put right again by heating the capillary.

[1] Scheel and Heuse, *Ber. d. deutsch. Physikal. Ges.*, 11, 10, 1909.

[2] *Ibid.*, 10, 85, 1908.

[3] Gaede, *Ann. d. Phys.*, 41, 289, 1913.

From all this it is obvious that the gauge must be cleared as far as possible of any gas which may be sticking to the walls of the tubes ; to do this it must be heated strongly after evacuation for at least an hour at 360° C. in the presence of a drying agent. This is very difficult with the gauge mounted on a flat board, as is customary. It is better to mount it on an iron stand, as shown in fig. 36. With this arrangement the gauge and air trap can be heated after evacuation, whilst the mercury is all kept in the reservoir by closing the needle valve. The mercury is let in after the completion of the heat treatment.

If the gauge is taken away from the tube system it should be put in connection with a little phosphorus pentoxide tube and sealed up. This will avoid a lot of trouble when the gauge is used again.

3. **The Absolute Manometer and Radiometer Gauges.** (a) *Principle*. The discovery of radiometric forces is due to Fresnel.[1] These forces are those exerted between two surfaces which are situated close together in a rarefied gas, when there is a difference of temperature between the surfaces. Crookes rediscovered the phenomenon with his radiometer with rotating vanes. A good deal of work has been done on these forces, primarily with regard to the measurement of the pressure of light. The radiometric forces make this measurement very difficult, and elimination of these forces has been tried in various ways and by suitable choice of gas pressure. At very low pressures these forces are of a very simple character, as was first shown by Knudsen.[2]

Let A_1 and A_2 (fig. 37) be two parallel plates in a rarefied gas, in which the pressure is sufficiently low so that the distance between the plates is small compared with the mean free path of the gas molecules. Let T_1 and T_2 be the absolute temperatures of the plates, and T that of the containing vessel. T may be also regarded as the temperature of the gas, except that between the plates. On the hypothesis that the energy exchanges between the impinging molecules and the plates

[1] A. Fresnel, *Œuvres*, **2**, 667–672. A description of Fresnel's experiment is given by Dunoyer, *loc. cit.*, p. 240.

[2] M. Knudsen, *Ann. d. Phys.*, **32**, 809–842, 1909.

are similar for both plates, p', the pressure between the plates, is related to the pressure p in the rest of the enclosure by the formula

$$p' = p\ \frac{\sqrt{T_1} + \sqrt{T_2}}{2\sqrt{T}}.$$

We shall see an important application of this formula further on, in the measurement of the pressures in an enclosure when different parts of the enclosure are at different temperatures.
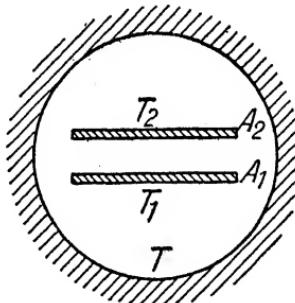
FIG. 37.

To apply the formula to the absolute manometer we shall suppose that the plate A_2 is at the same temperature as the rest of the enclosure. In that case we have

$$p' = \frac{p}{2}\left(\frac{\sqrt{T_1}}{\sqrt{T}} + 1\right) \qquad . \qquad . \qquad . \qquad (1)$$

Thus the two plates experience an excess pressure which tends to separate them if T_1 is greater than T. The value of the excess pressure is given by

$$F = p' - p = \frac{p}{2}\left(\frac{\sqrt{T_1}}{\sqrt{T}} - 1\right) \qquad . \qquad . \qquad (2)$$

If T_1 is less than T, the same pressure tends to bring the plates together.

In a qualitative way it is easy to see the reason for this phenomenon. The plate A_2, which is at the same temperature as the enclosure, receives, on the face opposite A_1, the impact of molecules coming directly from A_1, and therefore

with their mean velocity corresponding to T_1; the face turned away from A_1 is struck by molecules from the surrounding walls, and therefore with mean velocity corresponding to T. Thus, if T_1 is greater than T, the plate A_2 experiences a force tending to separate it from A_1. This argument [1] leads to a value of F which is the same as the value obtained by approximating in (2) for nearly equal values of T_1 and T, which is

$$F = \frac{p}{4} \cdot \frac{T_1 - T}{T} \qquad . \qquad . \qquad . \quad (3)$$

But it is not satisfactory, because, if we apply the reasoning to A_1 instead of A_2, since the molecules striking both sides of A_1 have mean velocities corresponding to T, it will experience no force. This cannot be true, so that the reasoning is incorrect.

From (2) we see that the force is independent of the nature of the gas; thus a gauge which measures the pressure by measuring this force is called an absolute manometer. This equation also shows that the plates need be neither flat nor parallel. The only important points are that their distance apart should be small compared with the mean free path of the gas molecules, and, as mentioned above, the similarity of the momentum exchanges at the two plates. The form of the surfaces is thus of no capital importance, and the natural thing is to choose them so that the resultant force per unit area on one plate can be conveniently calculated. However, for the measurement of fairly high pressures, the choice of plane parallel plates makes it easier to bring the plates closer together, and so fulfil the condition that their distance apart should be greater than the mean free path of the gas molecules.

Suppose that the manometer consists of two rectangular vanes of equal area A, symmetrical with regard to a torsion fibre which supports them. These vanes are at the same temperature as the enclosure, say T. They hang nearly parallel to two fixed plates of about the same size, which are at a different temperature T_1. Let r_0 and r_1 be the distances of the vertical sides of the rectangles from the axis, l the

[1] G. W. Todd, *Phil. Mag.*, 38, 381, 1919.

length of the vertical sides, θ the twist of the fibre, and C the constant of the fibre. Then

$$C\theta = 2\int_{r_0}^{r_1} Flx\,dx = Fl(r_1{}^2 - r_0{}^2) = 2AFr$$

where r is the distance of the middle of the vane from the axis. Thus we have

$$p\left(\sqrt{\frac{T_1}{T}} - 1\right) = \frac{C\theta}{Ar}$$

$$p = \frac{C\theta}{Ar} \cdot \frac{1}{\sqrt{\dfrac{T_1}{T}} - 1}.$$

C is usually got from the time of oscillation of the suspended system. If τ is the time period and I the moment of inertia about the axis of suspension,

$$\tau = 2\pi\sqrt{\frac{I}{C}}$$

and substituting

$$p = \frac{4\pi^2 I\theta}{Ar\tau^2} \cdot \frac{1}{\sqrt{\dfrac{T_1}{T}} - 1} \qquad . \qquad . \qquad . \qquad (4)$$

If T_1 and T are fairly high temperatures on the absolute scale, and if their difference is small,

$$p = \frac{8\pi^2 I\theta}{Ar\tau^2} \cdot \frac{T}{T_1 - T} \qquad . \qquad . \qquad . \qquad (5)$$

The angle θ can be measured by reflection from a mirror fixed to the suspended system.

Instead of using a torsion fibre it is possible to use a gold (or aluminium) leaf, as in simple electroscopes. The leaf is suspended very close to the fixed warm plate A, and as nearly parallel to it as possible. The manometers of this type are not really absolute, in spite of the simple geometrical arrangement, because the temperature of the moving system, which will be between that of the enclosure and the heated

plate, will be unknown. But in the case of the two vanes, the heat capacity of these is generally so large that, if the hot plates are heated only for a few seconds or for a minute at most, the temperature of the suspended system can be taken as unchanged, and thus equal to that of the enclosure, because there is so little conduction and convection at low pressures, and the radiated heat is inappreciable for small temperature differences. The thin gold leaf will have a very small heat capacity, so that the above will not hold for such an arrangement. In the torsion apparatus the temperature of the vanes can be measured, as was done by Knudsen in order to verify his assumptions. The manometer arranged in this way has too long a period for an instrument in general use.

(b) *Limits between which the Gauge can be used. Conditions suitable for Use.* A *priori* there would seem to be no low-pressure limit for the absolute manometer. It is possible to make them to read to about 10^{-7} mm. of mercury, which is as low as we can get at present. There will certainly be an upper limit for any particular case, which will be reached when the mean free path of the molecules is no longer large compared with the distance between the two surfaces. In published work on this gauge little precise information is given on this point.

According to Knudsen's measurements, equation (5) applies for hydrogen between 2 and 6 microbars, and for oxygen between 2 and 3·5 microbars. For higher pressures, with the same temperatures T_1 and T, the deviation θ increases much more rapidly than the pressure. Now the mean free paths of hydrogen and oxygen are in the ratio $\dfrac{16}{9}$, which is about $\dfrac{6}{3·5}$; so that, for pressures of 6 and 3·5 microbars respectively, the mean free paths of both hydrogen and oxygen molecules are 200 times as great as the distance between the plates in Knudsen's original model, the only model in which both T and T_1 were measured. The distance between the plates was 0·12 mm. This is a very small distance, and is difficult to realise between an oscillating system and a fixed

plate. In all later models the distance is much greater, being about a millimetre at least. Thus these later types are only " absolute " at pressures which are not greater than 0·3 microbar.

The lack of " absoluteness " is not only due to the fact that Knudsen's equations only apply when the distance between the fixed and moving plates is small compared with the mean free path of the gas molecules, but also because, when this is no longer true, the nature of the gas also affects the forces. This was discovered by West [1] in some work on the radiometric forces between the plate-glass wall of a vacuum chamber and a thin leaf (gold, copper, or aluminium), when these are heated with a powerful incandescent lamp which sets up a difference of temperature between them. Fig. 38 shows some of West's results. The abscissæ are logarithms of pressures, and the ordinates give the force per square centimetre of leaf for a difference of temperature of 1° C. between the leaf and the glass plate. According to the curves the law is no longer linear for pressures above 1μ, but this is not surprising, because the distance between the fixed and moving surfaces was much greater than in Knudsen's model. The curves also show that the force depends both on the nature of the gas and the distance between the surfaces. It is greater for the smaller distance, and greater for hydrogen than for air, in which the mean free path is smaller.

These curves do not give the direct results of the experiments, because these have to be reduced to the theoretical case of 1° C. difference of temperature between the surfaces.

To make this reduction West used the following formula :—

$$T = Q : \left[k \left(\frac{1}{d_1 + 2c\lambda} + \frac{1}{d_2 + 2c\lambda} \right) + 2R \right]$$

in which T is the rise of temperature of the leaf due to radiation, Q the heat the leaf loses per second by conduction and radiation through the gas, k the thermal conductivity of the gas, d_1 and d_2 the distances of the leaf from the two glass surfaces between which it is placed, R the emissivity of the

[1] G. D. West, *Proc. Phys. Soc.*, 27, 259, 1916; 31, 278, 1919; 32, 166, 1920; 32, 222, 1920.

leaf, λ the mean free path of the molecules, and c a coefficient depending on the nature of the gas.   The term $2c\lambda$ corresponds to a phenomenon similar to that of the sliding layer at the surface in Warburg's experiments. Q was found approximately by finding the rate of rise of a copper block placed in

<div style="text-align:center">

1. Hydrogen .   . ⎫
1′. Air   .   .   ⎬ Distance from strip to glass 0·29 cm.
2. Hydrogen .   . ⎪
2′. Air   .   .   ⎭   ,,   ,,   ,,   0·63 ,,
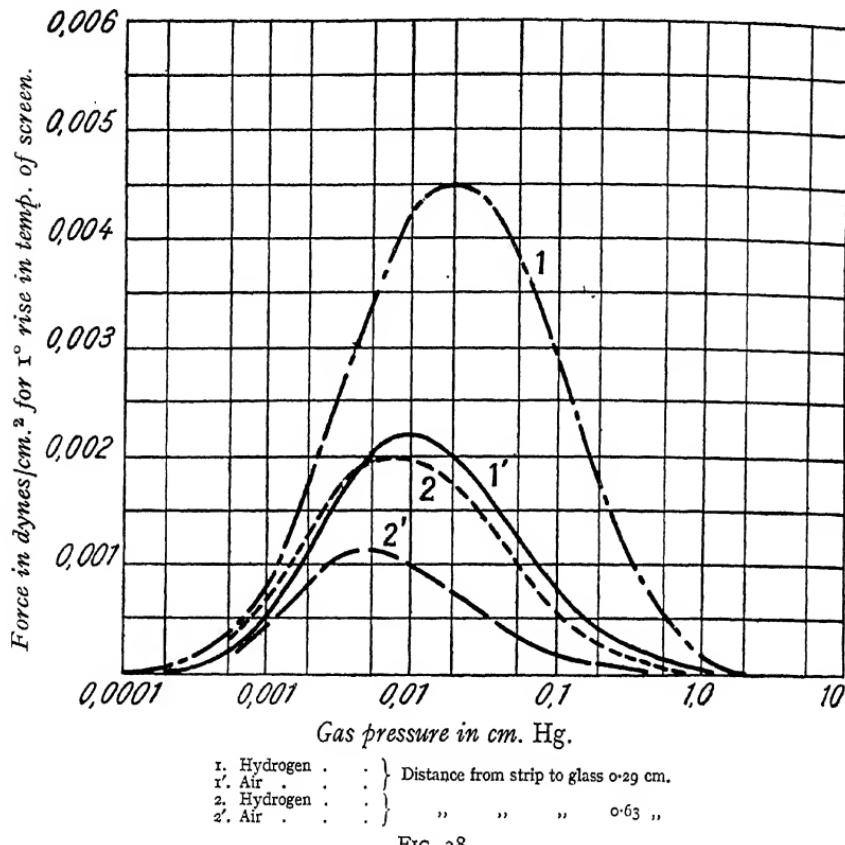
FIG. 38.

</div>

the experimental chamber and exposed to radiation from the lamp, with and without the leaf in between.   Thus the law of force is much more complicated than is shown by the curves in fig. 38, because the equilibrium temperature reached by the leaf depends on the pressure and properties of the gas.

To sum up, only a manometer like Knudsen's original model, in which the surface temperatures are actually measured, can be looked upon as an absolute manometer, and then only when

the distance between the fixed and moving plates is at most one two-hundredth of the mean free path of the gas molecules. References have already been given for descriptions of this manometer, and it will not be described more fully here, because it is not suitable for everyday measurement. The manometers described below are much more convenient, but they are not in any real sense absolute manometers, because the temperatures of the opposing surfaces are not measured. They must, therefore, be calibrated empirically ; this is usually done by using Boyle's Law. Except for very low pressures the calibration will only do for the gas with which it was made. The upper limit for this use depends on the distance between the two opposing surfaces, and is always lower than 1μ with all models now in use.

In spite of these restrictions, these so-called absolute manometers, which should perhaps be called radiometer manometers, are very useful instruments. The difficulty of interpreting readings for moderate pressures is also met with in gauges depending on thermal conductivity and on ionisation. For pressures less than 1μ they are quite satisfactory, and, since pressures greater than this can be measured with the McLeod gauge, there is little need to use them for such pressures as far as permanent gases are concerned. But vapours which cannot be measured with the McLeod gauge, such as mercury vapour, have pressures well within the range of the radiometer gauge. There remain the easily condensable gases, such as CO_2, NH_3, etc. Probably traces of these gases upset the measurements of the radiometer gauges as well as those of the McLeod.

(c) *Radiometer Gauges with Torsion Fibres.* The gauges with torsion fibres have suspended systems which can have quite an appreciable mass without having the time period inordinately long. This is a great advantage, as is seen from the preceding discussion, if the manometer is to be used as an absolute manometer. The temperature of the vanes will remain practically unaltered during the time of taking a reading, and the temperature of the heated plate is easily measured. But, on the other hand, these gauges have the great disadvantage of having practically no damping,

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the only appreciable damping at low pressures being that due
to the mechanical hysteresis of the fibre. Thus in practice
a magnetic damping arrangement is always used. These
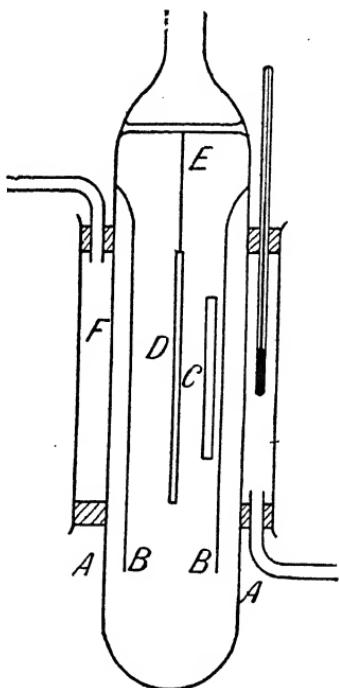
FIG. 39.

instruments are also obviously upset by vibration of the
table. This is felt particularly with molecular pumps which
always vibrate a little, because the pump must be joined to
the gauge by a short wide tube, which cannot be flexible.
But the gauge is all right with condensation pumps where
there is no vibration.

In his first paper on these gauges Knudsen gave short descriptions of various models. One of the simplest is shown in fig. 39.

Inside a glass tube A a second tube B is fused on, and this tube protects the mica slip D from molecules rebounding
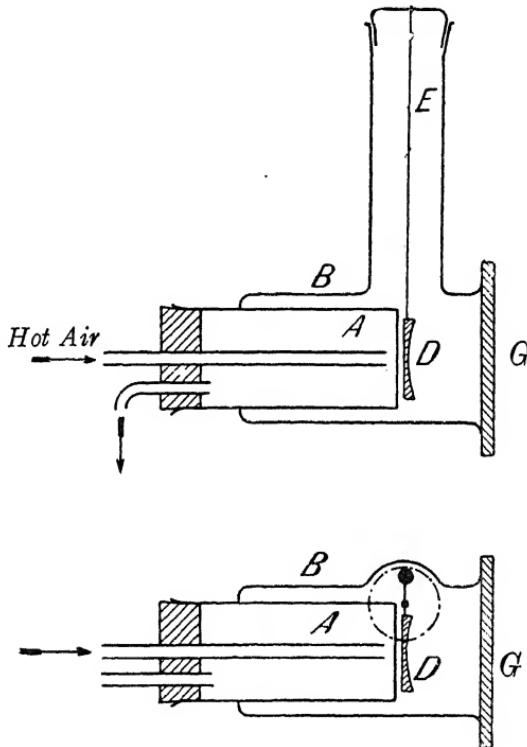
FIG. 40.

from A, except those which come in through a narrow window C cut in B. To make a measurement the walls of A are raised a few degrees in temperature by passing warm water through the jacket F. The mica slip is suspended from a torsion wire E, which must not, of course, be opposite the middle of C. A is about 14 mm. in diameter, and the opening C is 30 mm. long and 4 mm. wide.

Shortly after Knudsen published his first paper on these gauges the author [1] made a manometer of this type, which

[1] L. Dunoyer, *loc. cit.*, p. 242.

he showed before the Société de Physique, which was a nearer approach to an absolute gauge.

The vane D (fig. 40) was made of glass, and its thermal capacity was fairly large, so that its temperature could not change rapidly. It was suspended parallel to a flat glass surface, and about 1 or 2 mm. from it. A large displacement of the plate could be produced by blowing warm air against the flat plate. The instrument was handy, and even worked well for lecture experiments. It could be used as an absolute manometer for pressures which are higher than those for which Knudsen's model of fig. 39 would fulfil this requirement. This is on account of the small distance between the two plates. The face of the moving plate, which was turned away from the warm plate, was concave, and so could form an image of an incandescent filament on a fixed scale.

In a paper on the determination of the molecular weights of small quantities of gases and vapours, Knudsen [1] gave details of the construction of a manometer with torsion fibre, and another with an aluminium leaf. The first consists of a strip of mica G (fig. 41), suspended from a quartz fibre inside a wide tube A. Two glass plates H are fixed to the walls of A by thin glass rods ; the plates are placed one in front and one behind the mica strip, each covering half of it, and both being parallel to it. The edge of the mica is viewed through a microscope. The temperature of the tube is varied by circulating water through the jacket F. The water is warmed by warming a copper tube through which it passes when a measurement is being taken. On account of the small amount of conduction through their little glass supports, and also because of their big thermal capacity, the temperature of the fixed plates H can be assumed as invariable.

The temperature of the mica strip will also change much more slowly than that of the tube walls. If, after cold water has been passed through for some time, warm water is sent through, the mica strip moves towards the fixed plates. If the operation is reversed the mica moves away from the plates, and this seems to be the best way of making a measurement because the mica slip does not strike the plates. Knudsen

[1] M. Knudsen, *Ann. d. Phys.*, 44, 525–536, 1914.

does not give the sensitivity of this model.   It is easy to make it sensitive to 10^{-3} microbar.   It could be used for an absolute
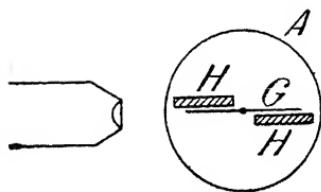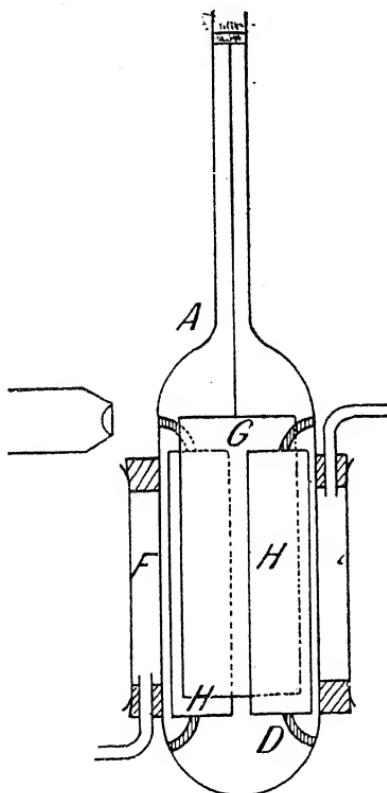
FIG. 41.

manometer if the temperature of the mica were known.   The temperature of the two sides of it may be different, as West's experiments (already described) would tend to show.

However, Knudsen calibrated this gauge by a method which is described further on.

Several instruments of this kind [1] have been made. They differ from Knudsen's model mainly in having metal strips heated by electric currents for the warm plate of the gauge. This allows bigger temperature differences to be set up, and thus the sensitivity is increased ; but it is not certain that
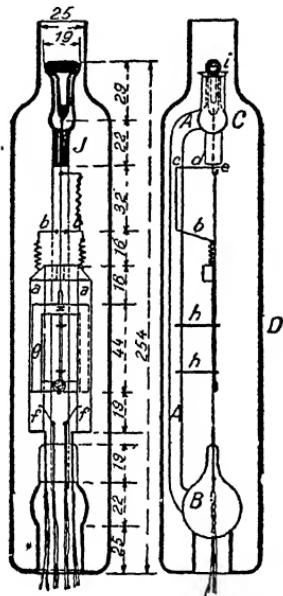
FIG. 42.

the accuracy of the results is greater, because the moving plate is made light to keep down the period of oscillation, and it is placed close to the warm surface in order to extend the range to higher pressures ; thus the temperature of the moving plate may vary fairly rapidly and to a different extent with different gases.

Fig. 42 shows Shrader and Scherwood's instrument. The whole arrangement is carried on a bent glass tube or rod A, which is fused at its lower end to the small bulb through which the current leads pass. Its upper end is fused on to

[1] Angerer, *Ann. d. Phys.*, 41, 1, 1913; Woodrow, *Phys. Rev.*, 4, 491, 1914; Schrader and Scherwood, *ibid.*, 12, 70, 1918.

the cup C, on the edges of which rests the little bar i which carries the suspension. This bar i is made from a tube, and a short piece of soft iron is sealed up inside it so that it can be turned by a magnet from the outside. The stem of the suspension hook e passes through a capillary tube, which guides it without holding it. The suspension is a tungsten wire of diameter 0·012 mm. The moving rectangular vane is cut from aluminium foil 0·076 mm. thick. The outside dimensions of the rectangle are 3·2 cm. by 4 cm., the width of the vane being 0·5 cm. The vane is stiffened by an aluminium wire passing through slits at the top and a hole at the bottom, into which the wire is hooked and fastened firmly. A mirror is fastened to the bottom of the vane by leaving a small projection at the lower edge of the leaf and cutting out small tongues from the leaf on each side. Two copper wires h, turned round at the ends, protect the suspended system from shocks when the gauge is moved about. The heated strips are of platinum foil, 0·018 mm. thick and 7·5 mm. wide, with a total length of 18 cm., bent as shown in the figure. The two ends of the foil are fused to the tungsten leads for the current, and these leads b are fused into the glass support and act as springs to stretch the foil. One of the leads, cd, is made long enough to touch the suspension hook, so that there will be no electrostatic field set up between the vane and the fixed foil. Two platinum wires f are fused on to the ends of the platinum foil as potential terminals in order to measure its resistance. The gauge is enclosed inside a glass tube D, about 5 cm. wide and 20 cm. long. All the joints are fused so that it can be evacuated and heated to get rid of surface gas.

The electrical connections for the gauge are shown in fig. 43.

The heating current is regulated by the variable resistance p, and its value read on the ammeter A. The resistance r_2 is kept constant at 10,000 ohms, and r_1 varied to obtain a balance of the sensitive galvanometer G. C is a calibrated Weston cell. The variation of resistance with temperature for the platinum is determined by preliminary experiments. If the time of reading is short and the gas is sufficiently rarefied, the temperature of the vane T may be considered

as the same as its initial temperature.   Knowledge of T_1, the temperature of the heated platinum, allows the application of equation (5).   Otherwise the gauge is calibrated experimentally.   With Shrader and Sherwood's actual instrument a deflection of 1 mm. on a scale placed at 1 metre indicates pressures from 10^{-5} to $5 \times 10^{-5}\mu$ for a temperature difference of 150° between the vane and fixed foil.   This sensitivity is quite good enough for the pressures we can get down to.

As a last model of this type we shall take that of L. F. Richardson.[1]   It consists of a flat box formed by two glass
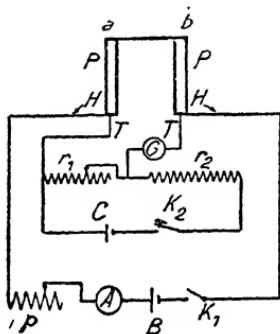
Fig. 43.

plates 10 cm. in diameter, cemented on to a glass ring 5·4 mm. thick.   Copper slabs are placed against the outer surfaces of the glass plates, and a difference of temperature of 10° is maintained between them.   Between the plates, and parallel to them, a strip of mica is suspended, its diameter being 35 mm. This vane is repelled by the hot plate towards the cold plate. The peculiarity of this instrument is the steady maintenance of the temperature difference.   This should make it easier to take direct readings and to take them more quickly.   Richardson's form of the apparatus seems rather complicated, and it would be interesting to try a simpler arrangement.   In his arrangement the vane carries a little flat spiral through which a current can be passed, one lead being the suspension wire and the other a loose wire from the bottom of the gauge.   A radial magnetic field between a rectilinear pole and a tubular pole concentric with it, both perpendicular to the plane of

[1] Lewis F. Richardson, *Proc. Phys. Soc.*, 31, 270–277, 1919.

the vane, brings the vane back towards its equilibrium position when a current is passed through the spiral. The size of the current and the difference of temperature between the plates enables the pressure to be calculated if Knudsen's law and certain hypotheses with regard to the temperatures of the two faces of the vane are assumed. But this method of calculation only applies to pressures below 2 microbars. However, the gauge was only tried for pressures below 0·4 microbar. An instrument of this type seems to be worth further study.

(d) *Radiometer Gauges with either Gold or Aluminium Leaves.* The torsion fibre manometers are inconvenient because of their slow damping, particularly at very low pressures. Usually a magnetic damping device is used with them, but this leads to complications, and often to changes of zero. Besides this trouble, these instruments are very susceptible to vibration, even with suitable damping devices, and this makes it difficult to use them with a molecular pump. Manometers in which the moving system is a thin metal leaf, like an electroscope leaf, damp down quickly without any external device, and the damping is still sufficient even at very low pressures on account of the small inertia of the leaf. This arrangement has been little used up to the present, on account no doubt of the uncertainty of the temperature of the leaf, and also because it can never be used as an absolute manometer. But if the instrument is calibrated by comparison it can be of great use, as Knudsen has shown in his paper on molecular weight determinations (*loc. cit.*). The instrument consists of a tube A (fig. 44), inside which a thick copper tube B is held by the little hooked springs b. The copper tube is cut right down the middle, as shown in the figure, and a little bar D is soldered on to the top part. An aluminium leaf about 0·5μ thick and 10 cm. long hangs from D. A small window is cut in the lower part of the copper tube, through which the leaf is viewed with a microscope. The temperature of the walls of A can be varied by passing water through the jacket F.

The temperature of the copper tube must remain constant throughout a reading ; this is the reason why it is supported

by the tiny springs. To cut down thermal exchanges still
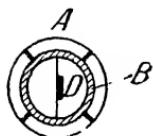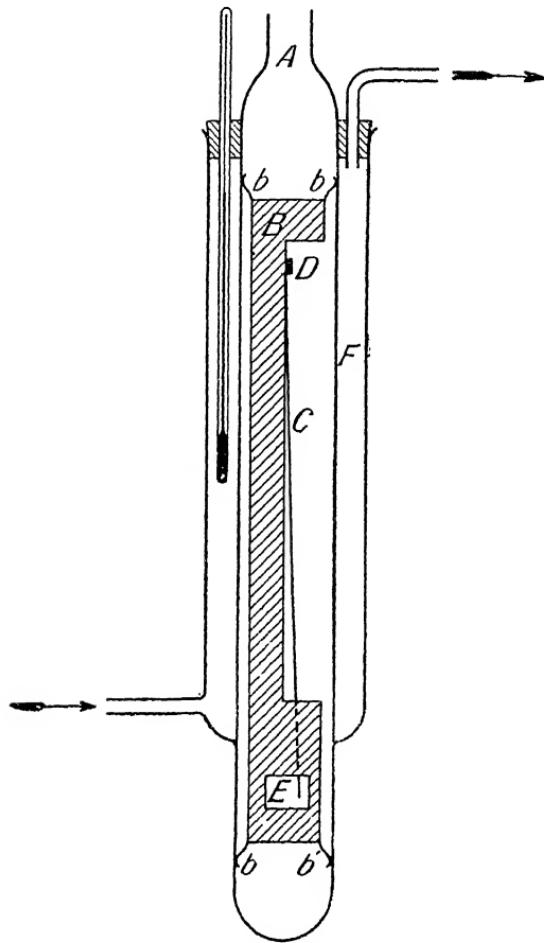
FIG. 44.

further, the tube A is silvered on the inner surface, except opposite the window E. If water which is colder than the

copper tube is circulated through F, the leaf moves away from the copper ; with water warmer than the copper it moves the other way. In taking a series of readings, hot and cold water are used alternately, so that the temperature of the copper remains unchanged.

With this instrument it is easy to get a deviation of half a millimetre at the end of the leaf for a pressure of 1 microbar, and a temperature difference of 1° C. between the glass wall and the metal tube. With a microscope it is easy to measure to $\frac{1}{200}$ of a millimetre, which, for a temperature difference of 50° C., corresponds to a pressure of 2×10^{-4} microbar.
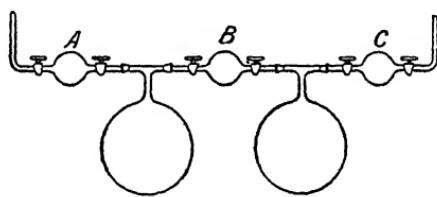
FIG. 45.

In practice temperature differences of 8° to 10° are most convenient. The author has verified that the relation between the temperature difference and the displacement is linear within the limits of experimental error.

A very similar gauge was made by Holweck to study his molecular pump. The main difference is that the leaf is viewed through a flat glass plate waxed on to the bottom of A, which is widened and ground flat. A little right-angled prism reflects the light into a horizontal reading microscope. It would be better to fuse the plate on instead of using wax. This is easily done in Pyrex.

(e) *Calibration.* Most radiometer gauges must be calibrated. In all cases this is advisable before they are used. But it must not be forgotten that the calibration only applies, for the higher pressures of its range at any rate, to the gas used in calibration. To calibrate a gauge a number of bulbs of known volumes are used, placed in series as shown in fig. 45. The small bulbs A, B, C can have volumes of

about 30 or 40 c.c., whilst the two big ones may be about 3 litres. The bulb A is joined to the pump and a mercury manometer, and C is joined to the radiometer gauge through a liquid air trap. The whole system is evacuated as far as possible, and then some gas (permanent) under known pressure is introduced into A alone. The tap which separates A from the pump is closed, and the gas is allowed to expand into the first big bulb and into B. B is then isolated, and then the gas in it is allowed to expand into the second big bulb and into C, which is then isolated, and then the gas in C is allowed to expand into the gauge. The gas pressure is calculated from Boyle's Law. The big bulbs are calibrated with water and the small ones with mercury. The volumes of the taps must also be taken into account.

4. **Gauges depending on the Thermal Conductivity of Gases.** If we have a bulb containing a gas, and a filament in the gas is maintained at a temperature higher than that of the walls of the bulb, a certain amount of energy, equal to that conducted by the gas, must be put into the filament to keep its temperature constant. The gas molecules striking the filament rebound, on the average, with more kinetic energy than they had before impact, and they share this energy with other gas molecules by collision with them, and the energy finally reaches the walls of the vessel.

As is well known, the kinetic theory of gases leads to the conclusion that the thermal conductivity and the viscosity of a gas are independent of the pressure. When the pressure is halved there is only half the number of molecules, but they travel twice as far. But when the pressure is so low that many of the molecules pass directly from the hot filament to the walls of the bulb without collision, the thermal conductivity will no longer be independent of the pressure. When the pressure is still further lowered, the number of molecules decreases, but the actual free path of any molecule is limited by the dimensions of the apparatus. Thus, when the mean free path becomes large compared with the size of the bulb, the thermal conductivity will decrease with the pressure, and so we have another means of measuring the pressure.

Although it is possible theoretically to calculate the heat transfer from the number of molecules per unit volume, just as it is possible to calculate the momentum exchange between surfaces at different temperatures or moving with different speeds, the phenomenon does not lead to the construction of an absolute manometer. The energy transfer evidently depends a great deal on the nature of impact and rebound at the filament. The author has already given an outline of our knowledge of this problem (*loc. cit.*), and since then little progress has been made, except in confirmation of the fact that the action is very complex.

But, even if the measurements were not absolute, it would be very useful to have an instrument of this kind, calibrated in the same way as the radiometer gauges, to measure the pressure of gases and vapours for which the McLeod gauge cannot be used. Unfortunately, even at low pressures, the heat loss of the filament depends on the nature of the gas. This is easily explained, because the contact conditions between gas molecules and solid surfaces certainly depend on the particular natures of both gas and solid. The values of the accommodation coefficient introduced in Knudsen's [1] theory show this very well. This coefficient, a in the table, is the ratio of the heat which actually passes into the gas from the solid, to the amount which would pass if the molecules coming into contact with the solid came into temperature equilibrium with it. The following are the values of a measured up to the present :—

Knudsen $\begin{cases} \text{H}_2 \text{ in contact with polished} \\ \quad\text{platinum or glass} \quad . \quad . \quad a \qquad = 0.26 \\ \text{CO}_2, \text{N}_2 \quad . \quad . \quad . \quad a \qquad = 0.87 \end{cases} \begin{matrix}\text{temp. near} \\ \text{atmospheric.}\end{matrix}$

Soddy and $\begin{cases} \text{H}_2 \text{ in contact with platinum} \quad a_{-100}°\text{C.} = 0.25 \quad a_{+200}°\text{C.} = 0.15 \\ \text{He} \quad . \quad . \quad . \quad a_{-100}°\text{C.} = 0.49 \quad a_{+100}°\text{C.} = 0.37 \end{cases}$
Berry.[2]

Langmuir [3] $\begin{cases} \text{H}_2 \text{ in contact with tungsten} \quad a_{+1500}°\text{C.} = 0.19 \\ \text{N}_2 \quad . \quad . \quad . \quad a_{+1500}°\text{C.} = 0.60 \end{cases}$

Thus a varies with the temperature, the nature of the gas, and that of the surface. It is also probable that the influence of

[1] M. Knudsen, *Ann. d. Phys.*, **34**, 593, 1911 ; L. Dunoyer, *loc. cit.*

[2] Soddy and Berry, *Proc. Roy. Soc.*, **84**, 576, 1911.

[3] Langmuir, *J. Am. Chem. Soc.*, **37**, 425, 1915.

the latter is due more to its physical state than to the nature of the elements in the surface. According to Langmuir there is always a layer of gas sticking to the surface, and the molecules rebound from this layer. As regards the temperature, a seems to decrease with rise of temperature of the solid.

Thus gauges depending on the thermal conductivity of
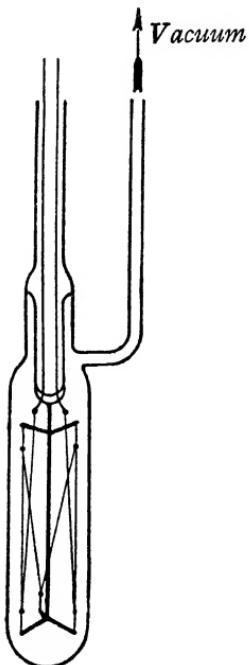
FIG. 46.

gases can never be used as absolute manometers because of their dependence on the nature of the gas. But they are very useful in spite of this limitation.

(a) *The Pirani-Hale Gauge.* The first pressure gauge using the heat loss of a filament as a measure was due to Pirani.[1] Hale's form of the gauge [2] is very similar to an ordinary incandescent lamp in construction, but the filament is not heated up to redness. The only precautions necessary

[1] *Verh. d. deutsch. Physik. Ges.*, **24**, 684–694, 1906.
[2] *Trans. Am. Chem. Soc.*, **20**, 243–258, 1911.

in construction are to keep the filament tight, so that the distance between it and the glass walls is constant, and to arrange for minimum heat losses through the filament supports. The bulb is totally immersed in a constant temperature bath. In practice a good tungsten filament lamp, with a tube let in near the base, will do quite well.

Obviously the filament should have as big a temperature coefficient as possible to make it very sensitive to temperature changes, since it has to be kept at constant temperature. In Hale's instrument the filament was of pure platinum wire 0·028 mm. in diameter and 45 cm. long. The temperature coefficient was 0·00376 per degree. The filament was welded in the arc to short pieces of platinum wire, which were fused into three little glass rods at the end of the central rod, and into two similar glass rods at the top end. The bulb was 11·4 cm. long and 3·2 cm. in diameter. It was thus easily immersed in a thermostat with the current leads insulated. The tube containing the leads was packed with cotton wool to stop water from condensing there. The thermostat was kept at or near 0° C., whilst the filament was maintained at temperatures between 100° and 125° C.

(b) *Instructions for Use and Calibration.* Since this gauge must be calibrated by comparison, all that is necessary is to keep the difference of potential between the ends of the filament constant and read the current. The higher the pressure, the greater the conductivity, and thus the greater the current. Measurements may also be made by keeping the current constant and measuring the change of resistance of the filament. The lower the pressure the greater the resistance. Hale recommends the latter procedure. But since the calibration is only strictly applicable under the same conditions as those obtaining when it was determined, it should be better, as Campbell [1] has pointed out, to keep the temperature of the filament, and therefore its resistance, constant.

The gauge is placed in one of the arms of a Wheatstone network (fig. 47), the other three arms being composed of resistances with very low temperature coefficients (of man-

[1] N. R. Campbell, *Proc. Phys. Soc.*, 33, 287–296, Aug. 1921.

ganin). One of the resistances, R_1, is variable, and it is adjusted so that the galvanometer G will show no deflection when the resistance of the manometer corresponds to the filament temperature chosen. The current is got by tapping off from the resistance P. The voltmeter V is the real measuring instrument. The bigger the pressure the bigger will be the voltage indicated by V.

To use Hale's procedure an ammeter is used instead of
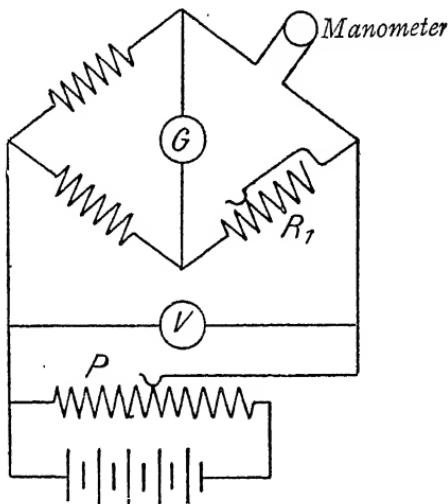
FIG. 47.

a voltmeter, and it is placed in series with the battery and the resistance P. P is varied to keep the current constant, and R_1 varied to keep the bridge balanced. Thus the readings are got from the resistance of R_1.

With Campbell's arrangement the calibration curve plotted is not p the pressure against V the voltmeter reading, but p against $\dfrac{(V^2 - V_0^2)}{V_0^2}$, where V_0 is the voltmeter reading corresponding to the lowest attainable pressure. The heat losses along the current leads, and by radiation and by conduction across the gas, are nearly proportional to the excess temperature of the filament over that of the walls of the bulb. Also the total energy loss must be proportional

In order to obtain the calibration curves, all that is neces-
sary is to join up the gauge to a pump and evacuate as far

$$\frac{V^2 - V_o^2}{V_o^2}$$

Pressure in mm.

Hydrogen ——— Water — — — Air - - - - - -
Carbon Monoxide ⎫
Carbon Dioxide ⎬ — — — — — — — — —
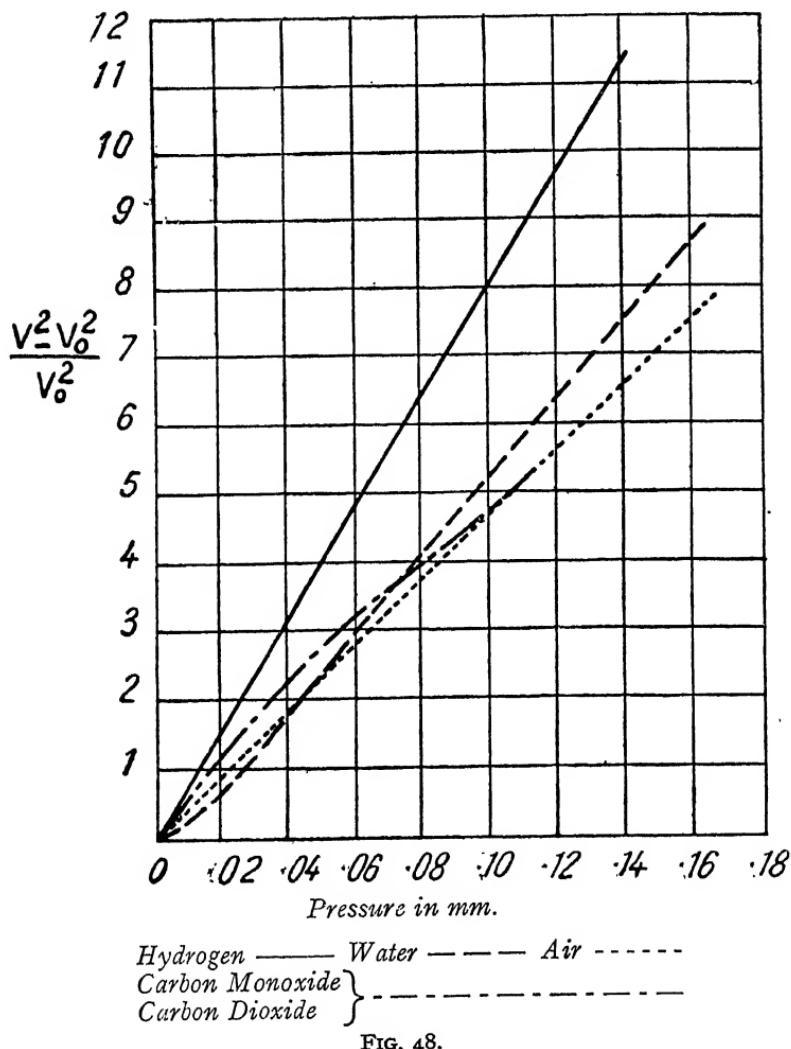
FIG. 48.

as possible (clearing off surface gases from the bulb and
filament by heating strongly), and then introducing into the
manometer different gases at known pressures. Fig. 48
gives Campbell's curves, in which the abscissæ are pressures

and the values of the ratio $\frac{(V^2 - V_0^2)}{V_0^2}$ are ordinates. They were obtained for air, hydrogen, carbon monoxide, and carbon dioxide, the pressures being measured with a McLeod gauge. This is perhaps the reason why the carbon dioxide curve seems anomalous; but this curve practically coincides with the carbon monoxide curve, and the McLeod gauge should give exact results for the latter gas. The water curve was got by introducing hydrogen and oxygen into the tube system and measuring their pressures and then causing part of the gases to combine by an incandescent platinum filament. The water vapour formed was condensed in a suitably cooled side tube (cooled to $-95°$ C.), and the new pressure measured; the gases are then drawn off as completely as possible by the pump, after which the water is allowed to vaporise. Perhaps the curving inwards of the water graph near the origin was due to condensation of a little vapour on the walls of the gauge, when the pressure of the residual gases was being measured.

During calibration with a McLeod gauge it is of course necessary to put in a mercury vapour trap surrounded by liquid air (like that in fig. 25). The trap is placed near the gauge which is being calibrated. It is clear that in practice the trap would be useless if a mercury pump were used, and there would be no need to get rid of the mercury vapour.

For calibration a system of bulbs of known volumes, as shown in fig. 45, would do instead of a McLeod gauge. This method would probably be the better one.

It will be noticed that the curves in fig. 48 are not drawn to enable low pressures to be read off. The curves were drawn for a method of microanalysis of gases. This method is described in Chapter III. As a matter of fact, except in special cases where the nature of the gas in the gauge is known, some such method of gas analysis is absolutely necessary with this type of gauge, because the readings depend on the nature of the gas. If the gauge is used without the gas being analysed, errors of the order of 20 per cent. in the pressure may be made: this is the actual difference in readings for the same pressures of air and hydrogen. Gauges

of this type are less sensitive than radiometer gauges ; they will hardly measure pressures below 0.01μ. On the other hand, fig. 48 shows that they can be used for very much higher pressures.

According to Campbell there is little difference in the time of one reading between a gauge of the Pirani type and a McLeod gauge, because in the former it takes about a minute for the establishment of thermal equilibrium. However, if the gauge is kept in ice or other constant temperature bath, and if a constant current is maintained through the filament there, except for very rapid pressure changes, equilibrium would be constantly maintained, and the gauge would give continuous registration, which is an important advantage in practice.

5. **Ionisation Gauges.** If an electron current is produced in a gas at low pressure between a hot filament and an anode, the electrons will ionise the residual gas if their velocity is large enough—that is, if

$$\tfrac{1}{2}mu^2 > Ve$$

where u is the velocity of the electrons, e their charge, m their mass, and V the ionisation potential of the gas. The positive ions thus produced can be gathered by a collector electrode, and the intensity of this ionisation current may be used as an indication of the pressure. It is obvious that each gas would require a separate calibration in such a gauge.

Buckley,[1] and then Misamichi So,[2] were the first to study gauges founded on this principle. Misamichi So's instrument had three tungsten filaments, all V-shaped, set up in parallel planes—one of them was raised to incandescence ; one was used as the anode for the electron current ; and the third served as a collector electrode for the position ions, and was, therefore, maintained at a potential lower than that of the lower potential end of the hot filament. According to Buckley the position and shape of the electrodes does not matter very much. However, Dushman and Found [3] have shown that one particular mode of construction exists

[1] *Proc. Nat. Acad. Sci.*, **2**, 683, 1916.
[2] *Proc. Physico-Math. Soc. Japan*, **1**, 76, 1919.
[3] S. Dushman and C. G. Found, *Phys. Rev.*, **17**, 7–19, 1921.

for which there is a linear relation between the ionisation current and the pressure. This is obviously an important advantage, and it is probably due to the fact that one of the electrodes is a cylinder surrounding the two others. If the hot filament is not surrounded in this way, charges on the glass walls complicate the action of the gauge.

Dushman and Found's gauge has been used in practice at the laboratories of the General Electric Co. (America), and so it will be described rather fully.

(a) *Description, Mounting, and Preparation of the Instrument.* The gauge is very similar to the three electrode valves used in wireless practice.

The glass tube A (fig. 49) is about 12 cm. long, and has a diameter of about 4 cm. The two filament electrodes B and C are supported from the same end, as shown in the figure. Each of these has two current leads. The other electrode D is fixed in from the other end, and has only one lead to it. A side tube is fitted in to join the gauge to the vacuum apparatus.

The inner electrode C is a tungsten filament of diameter 0·125 mm., wound in a double spiral of five turns on a cylinder of diameter 2·25 mm. The outer filament B is made of the same wire in the form of three turns of double spiral on a cylinder of diameter 3·65 mm. D is a hollow cylinder of molybdenum, 12 mm. in diameter and about 12 mm. long.

These are the details as far as given by Dushman. It seems as if certain types of commercial valves would do quite as well.

The wiring up of the gauge can be done in two ways. The first way is shown in fig. 49. In this arrangement the inner filament C is the hot cathode, the heating current coming from E through the regulating resistance R. B is the anode, and the field for the electron current is produced by the battery F, this current being measured by M.

The potential of B is of the order of 125 to 250 volts, and the electron current from 0·5 to 20 milliamperes. The cylinder D is the collector electrode. By means of the battery H it is brought to a potential below that of the negative end of the hot filament. The positive ion current is measured by the galvanometer G, which should be much

more sensitive than the milliammeter.   We shall call this the external collector arrangement.
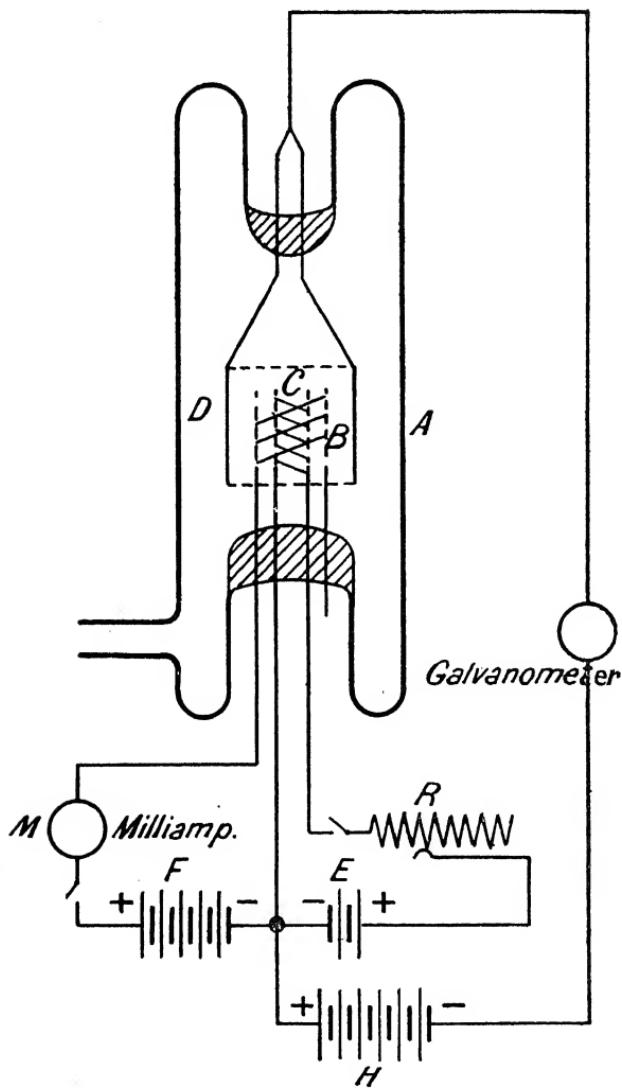
FIG. 49.

The second set-up will be called the internal collector arrangement.   The outer filament B is the electron source in this case, D is the anode, and C is the collector electrode.

This arrangement is less sensitive than the other, but it has some advantages, as will be seen later.

Before the gauge can be used the whole of the interior, metal and glass, must be cleared of surface gases. The following treatment is applied to remove these: " After starting the exhaust with a Langmuir condensation pump, the gauge is heated in an oven to 360° C. for at least one hour. This removes practically all the water vapour. In order to free the molybdenum cylinder of gas, it is made the anode with respect to the outer spiral, which is used as hot cathode. The temperature of the latter is adjusted by varying the current through it until the electron emission is about 100 milliamps. With an anode voltage of 250 volts this corresponds to an energy input of 25 watts (5·5 watts per sq. cm. of anode approximately), and is sufficient to raise the temperature of the cylinder to a red heat. The gas liberated in consequence of this electronic bombardment causes a blue glow in the gauge, which disappears as the exhaust proceeds. The electron emission is then gradually increased until it finally reaches about 400 milliamps., corresponding to 100 watts energy input (22 watts per sq. cm.). With this amount of energy the cylinder runs at a bright red heat (about 1900 Abs.), and the elimination of gas occurs very rapidly. Momentarily the energy input may be increased to 150 watts ; but there is serious danger, under these conditions, of melting the cylinder locally. After this treatment the anode is usually quite bright, and all traces of oxide on its surface have disappeared."

To clear the gas from the conductors which support the spiral filaments, one of these is made the anode and the other the hot cathode. With an energy input of 15 to 20 watts, the wires are brought to a bright red, and gas comes off freely. These conductors must be cleared of gas before the gauge is used, otherwise there will be continual emission during each measurement.

(b) *Investigation of Running of the Instrument.* Before undertaking the real calibration, the following were tried : the influence of the potential of the collector electrode on the ionisation current ; the influence of the anode potential

with constant electron current ; and the influence of the size of the electron current with constant anode potential. These were tried with the external collector arrangement, with argon at a pressure 1·85 microbars. Before the argon was let in, the residual gas pressure, measured by the ionisation current, was less than one-thousandth of the pressure of the argon. It is obviously necessary to take the greatest care to eliminate mercury vapour and any other easily condensable vapour.

Influence of Collector Voltage. This has little effect for voltages from 0 to −22 (0 is the potential of the negative end of the hot filament). Thus the collector potential was fixed at −22 volts throughout.

Influence of Anode Voltage with Constant Electron Current. The electron current was kept at 0·5 milliamp., and the ionisation current was practically zero until the anode potential reached 30 volts ; it then increased rapidly and then more slowly. The highest voltage was 250. The change can be represented by the empirical formula

$$i = i_0(1 - e^{-B(V - V_0)})$$

i being the ionisation current correspond to an anode potential V, i_0 to V_0.

Influence of Electron Current, Anode Voltage constant. The anode voltage was kept at 250 ; and the ionisation current was measured for various values of the electron current, this being varied by changing the temperature of the hot filament.

Fig. 50 shows that the relation is linear with electron currents from 0 to 10 milliamps. At bigger currents this no longer holds. This is no doubt due to the fact that electrons pass through the anode filament and are then drawn back on to it. The bigger the space charge caused by electrons outside the anode filament, that is, the greater the emission, the smaller is the path of the electrons repelled by the collector electrode (at −22 volts) outside this space ; thus the ionisation current will increase at a slower rate than before.

When the internal collector arrangement was used, the linear law was followed quite well up to electron currents of 20 milliamp., as is shown in fig. 51.

But in this case the ionisation current, for a given electron

current, was only one-third of the value in the other case. Thus the sensitivity of this arrangement will be also one-third that of the first.

These investigations led to the choice of the following conditions for calibration :—

Anode potential, 250 volts.

Anode current in milliamperes.
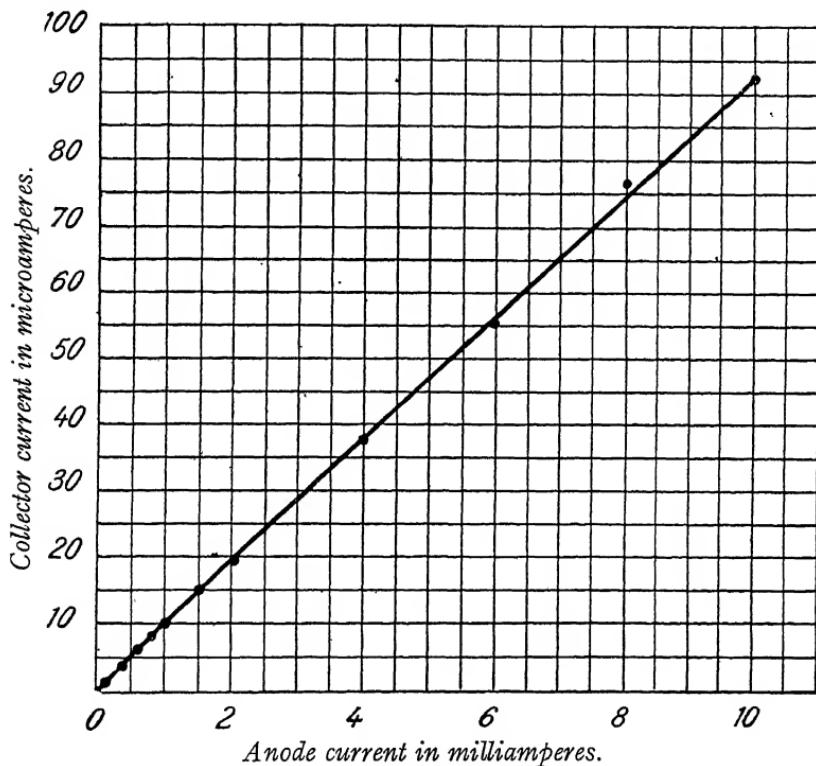
FIG. 50.

Collector potential, —22 volts.

Maximum electron current, 20 milliamps.

The sensitivity could be made to vary continuously by changing the electron current, the linear law enabling comparison to be made of measurements at different sensitivities. Two sensitivities will suffice, corresponding, for example, to electron currents of 0·5 and 20 milliamps. for the pressure range 0·0001 to 50 microbars.

(c) *Calibration.* To calibrate the instrument at pressures above 1 microbar either the set of bulbs of known volumes
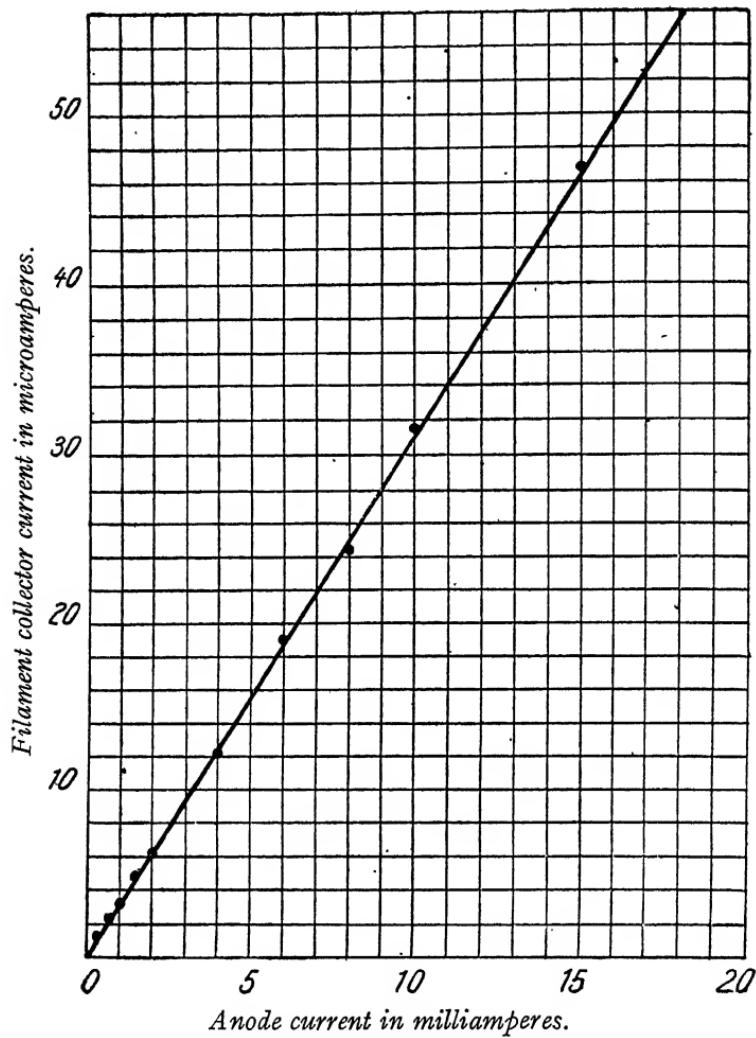
FIG. 51.

or a good McLeod gauge can be used. With the McLeod a liquid air trap for mercury vapour is necessary. Dushman and Found used a McLeod gauge, and used pure argon as the gas in the tube system.

For fixed values of anode potential and electron current, the ionisation current is found to increase at first proportion-
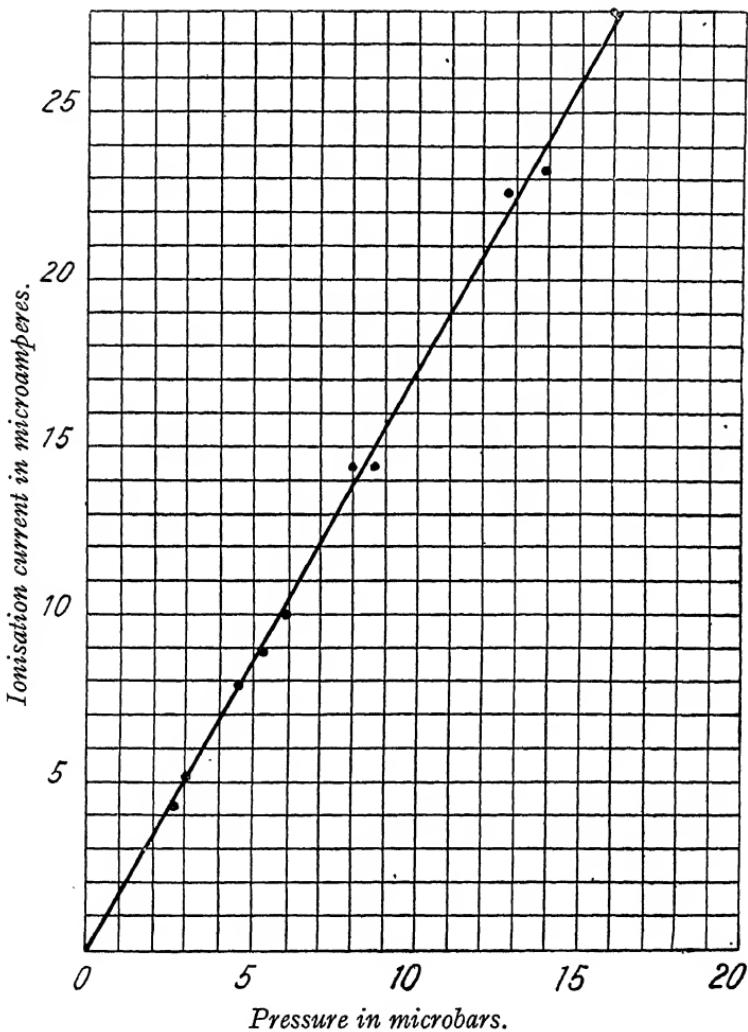
FIG. 52.

ally with the pressure, but beyond a certain pressure the ionisation current increases more rapidly than the pressure, due, no doubt, to ionisation by collision. This limiting pressure for proportionality is lower the greater the electron

current. For example, with an electron current of 5 milliamps. the proportionality holds up to 1·2 microbars; with 15 milliamps. electron current the limit is a little below 1 microbar ; and for 25 milliamps. the limit is only 0·4 microbar. Thus, in order to measure pressures between 1 and 50 microbars, the electron current should not be greater than 0·5 milliamp. (with anode voltage 125). Fig. 52 shows a part of the calibration curve. It shows that under these conditions 1 microamp. corresponds to 0·7 microbar of argon.
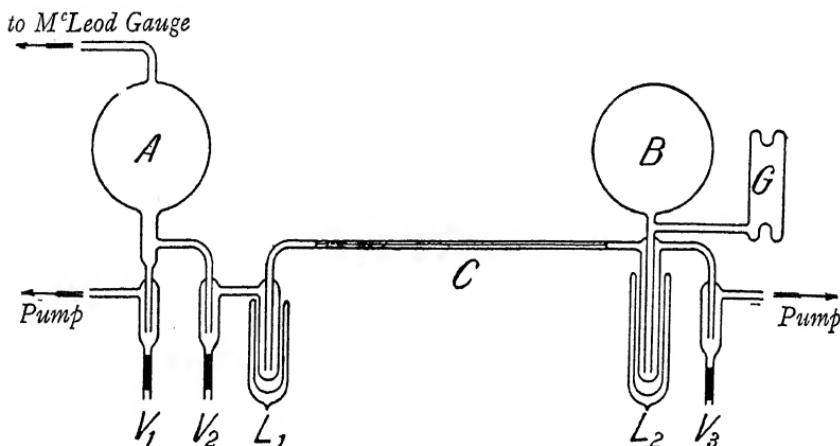
FIG. 53.

For pressures less than 1 microbar, bigger electron currents can be used. Dushman and Found recommend 20 milliamps. (with anode voltage 250). However, according to the results given above, it seems that the linear law would no longer be followed near 1 microbar with this electron current. The method of calibration for very low pressures is worth mentioning. We have seen that for such pressures the McLeod gauge is useless. The McLeod is therefore used only for measuring the pressures of argon in a big 3-litre bulb A (fig. 53), these pressures being from 10 to 20 microbars.

The ionisation gauge G is joined to a second bulb B, whose volume is about equal to that of A. These two bulbs are joined by a long, fine capillary C (130 cm. long and about 0·7 mm. bore) ; between the two are also the mercury valve V_2 and the liquid air traps L_1 and L_2. First the whole apparatus

is evacuated as far as possible, and the gauge is given the heat treatment described above. The valves V_2 and V_3 are then closed, isolating the gauge, and the pump and L_1 and L_2 are immersed in liquid air. The ionisation current should then remain constant and very small. Argon is introduced into A, and its pressure is measured by the McLeod gauge; then V_1 is closed and V_2 opened. The gas then flows through the capillary under the very small pressure difference, and the change of ionisation current with time is noted. The ionisation current increases proportionally with the time for more than an hour.

The rise of pressure in B can be calculated from Knudsen's law of flow at low pressures.[1] Let D be the diameter of the tube and L its length, P_A and P_B the pressures in A and B at time t, and P the mean pressure of the stream of gas

$$P = \frac{P_A + P_B}{2},$$

v the volume flowing per second, measured at the mean pressure, ρ the density of the gas under a pressure of 1 microbar, and Q the mass flowing per second, then

$$Q = v\rho P.$$

Knudsen has shown that, at pressures low enough for the mean free path to be great compared with the diameter of the tube,

$$vP = T(P_B - P_A).$$

T is the product of the mean pressure, and the volume flowing per second under a pressure difference of 1 microbar. The volume is measured at the mean pressure, and T is independent of this pressure.

$$T = \frac{\pi}{3\sqrt{2}} \frac{D^3}{L} \frac{1}{\sqrt{\rho}}.$$

So that

$$Q = \frac{\pi}{3\sqrt{2}} \frac{D^3}{L} \sqrt{\rho} (P_A - P_B).$$

[1] M. Knudsen, *Ann. d. Phys.*, **28**, 81, 1909; L. Dunoyer, *loc. cit.*; also Chapter III of this book.

But if V is the volume of the bulb B and the gauge, then the arrival of Q produces an increase of pressure dp such that

$$Qdt = V\rho dp.$$

So that

$$\frac{dp}{dt} = \frac{\pi}{3\sqrt{2}} \cdot \frac{D^3}{L} \cdot \frac{1}{\sqrt{\rho}} \cdot \frac{P_A - P_B}{V}.$$

But during the calibration P_A is practically constant and P_B is negligibly small compared with P_A.

Thus, approximately,

$$\frac{1}{P_A} \cdot \frac{dp}{dt} = \frac{\pi}{3\sqrt{2}} \cdot \frac{D^3}{L} \cdot \frac{1}{\sqrt{\rho}} \cdot \frac{1}{V}.$$

In Dushman's experiments this was equal to $0 \cdot 831 \times 10^{-5}$: that is, for each microbar of pressure in A, the increase of pressure in B was $0 \cdot 831 \times 10^{-5}$ microbar per second, or $4 \cdot 98 \times 10^{-4}$ microbars per minute.

Since $\dfrac{di}{dt}$ (i is the ionisation current) and $\dfrac{dp}{dt}$ are constants, we should have

$$\frac{dp}{dt} : \frac{di}{dt} = k. \qquad p = ki.$$

The table below gives the results obtained with an electron current of 20 milliamps., and an anode potential 250 volts, for various values of P_A.

$\dfrac{dp}{dt}$ microbars per min. calculated.	$\dfrac{di}{dt}$ microamps. per min. observed.	$h \cdot \dfrac{\text{microbars}}{\text{microamps.}}$
0·0116	0·85	0·0145
0·0112	0·91	0·0124
0·0081	0·58	0·0140
0·0071	0·52	0·0133
0·0060	0·47	0·0128
0·0059	0·44	0·0132
0·0057	0·39	0·0146
0·0056	0·52	0·0108

mean 0·0132

From these results Dushman considers that the law of proportionality holds for an electron current of 20 milliamps.,

each microamp. of ionisation current corresponding to 0·0132 microbar of argon. The author thinks that with a galvanometer sensitive to 10^{-8} amperes the gauge could be used, by extrapolation of the linear law, to measure 10^{-4} microbars.

It seems that, from Dushman's own results, the linear law, for an electron current of 20 milliamps., does not hold for pressures greater than 0·7 microbar. For higher pressures a smaller electron current must be used. If only two values, 20 and 0·5 milliamps., are used, it would seem that pressures round about 1 microbar are a little high in one case and a little low in the other.

All the above results were got with the external collector arrangement. If the internal collector arrangement is used (paragraph 5 (a) above), the linear law is true up to 20 milliamps. (fig. 51) ; the sensitivity of the gauge is then reduced to one-third, but it would then be easier to get the electron current to suit the pressure to be measured. Moreover, for anode voltages of 150 there is no change with variation of this voltage (the cylinder is the anode in both arrangements). This is no doubt due to the fact that with this arrangement the path of the electrons is not dependent on the anode voltage, as is the case with the external collector arrangement.

(d) *Use of the Gauge with Different Gases.* The experiments described above were made with argon. The same authors have given in a previous note [1] some results obtained with the ionisation gauge for other gases. At equal pressures, for the same electron current and the same anode potential, the ionisation current increases with the number of electrons in the molecule. This is got by multiplying the number of atoms of each kind by the atomic number of the element. Thus the number of electrons per molecule is 2 for H_2, 16 for O_2, 14 for N_2, 18 for A, 80 for Hg, 53 for I, 10 for H_2O, 186 for HgI_2. But the proportionality between ionisation current and number of electrons is not a general rule ; hydrogen, helium, and neon are exceptions. Further work is required on this point.

On account of the difference for different gases the practical use of the gauge is very limited. It has been used to

[1] S. Dushman and C. G. Found, *Journ. Frank. Inst.*, **188**, 819, Dec. 1919.

investigate the changes of pressure in incandescent lamps and
hot cathode devices after sealing off from the pump. At the
present state of our knowledge of its working it is only useful
for the comparison of lamps or valves during some stand-
ardised process. It has, however, the great advantage of
continuous registration.

6. **Manometers depending on the Viscosity of Gases.** The
viscosity of a gas, like the thermal conductivity, is independent
of the pressure so long as the mean free path of the gas
molecules is small compared with the distance between the
surfaces at different velocities. When the pressure is lowered
until this no longer holds, the transfer of momentum between
the two surfaces by the gas molecules decreases with the
pressure. Thus instruments for measuring pressure can be
made depending on the transfer of momentum, if the pressures
are low enough. These instruments are described after those
depending on thermal conductivity, because they have not
been used much up to the present, so that their interest is
rather theoretical than practical.

(a) *Experiments with an Oscillating Disc.* If there are
two plane parallel surfaces at a distance d apart, and one of
them moves, in its own plane, with a velocity u relative to the
other, the transfer of momentum per unit area per second
to the latter is given by

$$B = \frac{\eta u}{d}$$

if the mean free path of the gas molecules is small compared
with d. η is the viscosity, and is defined in this way. B is
therefore the tangential force per unit area of the fixed plane,
and is independent of the pressure in this case.

When the pressure is lowered so that the mean free path is
no longer small compared with d, Kundt and Warburg [1]
showed, in a historic paper, that the tangential force is given
by

$$B = \frac{\eta u}{d + 2\delta}$$

[1] Kundt and Warburg, *Pogg. Annal.*, 155, 340, 1875. See also M. Bril-
louin, *Leçons sur la viscosité des gaz.*

where δ is inversely proportional to the pressure, and therefore proportional to the mean free path L ;

$$\delta = aL,$$

where a is a coefficient which depends on the nature of the gas and the state of the surface. δ is the correction for slipping, because the apparent viscosity decreases owing to the slipping of gas molecules over the planes. If δ becomes large compared with d, that is at sufficiently low pressures, the value of B can be got from

$$B = \frac{\eta u}{2\delta} = \frac{\eta u}{2aL}.$$

From the kinetic theory of gases we can express $\dfrac{\eta}{L}$ in terms of the density of the gas ρ and the average velocity of the molecules. So that

$$\frac{\eta}{L} = k\rho\Omega$$

where k is a numerical coefficient nearly equal to $\frac{1}{3}$. But if M is the molecular weight and p and T the pressure and absolute temperature

$$\rho = \frac{Mp}{RT}$$

and

$$\Omega = \sqrt{\frac{8}{3\pi}}\sqrt{\frac{3RT}{M}} = \sqrt{\frac{8RT}{\pi M}}$$

so that

$$B = Apu\sqrt{\frac{M}{RT}} \qquad \cdot \qquad \cdot \qquad \cdot \qquad (1)$$

where

$$A = \frac{k}{a}\sqrt{\frac{2}{\pi}}.$$

Thus B is proportional to the pressure. Kundt and Warburg verified this experimentally with a plane glass disc suspended from its centre by a torsion fibre. The disc was situated between two fixed horizontal flat plates, and the

distance between the plates was a few millimetres. The whole arrangement was placed in an evacuated bell jar, and the disc was made to oscillate by means of a piece of soft iron fixed to the suspension fibre. The damping of the oscillations was read by means of a mirror and lamp and scale.

The logarithmic decrement is proportional to the pressure p. If $\dfrac{da}{dt}$ is the angular velocity of the disc at any given time, the viscous couple opposing the rotation is given by

$$\Gamma \frac{da}{dt} = 2\int_0^r Ap\sqrt{\frac{M}{RT}}\, r\, \frac{da}{dt} \cdot 2\pi r^2 dr = \pi r^4 Ap \sqrt{\frac{M}{RT}} \cdot \frac{da}{dt}.$$

If a_0 and a_n are the amplitudes of the first and the $(n+1)^{\text{th}}$ oscillations, and τ_0 and τ_n the times of the first and $(n+1)^{\text{th}}$ transits through the equilibrium position, then

$$\frac{\Gamma}{2I} = \lambda = \frac{1}{\tau_n - \tau_0} \cdot \log_e \frac{a_0}{a_n} \qquad . \qquad . \qquad (2)$$

where I is the moment of inertia of the disc. Therefore

$$p = \frac{2I}{\pi r^4 A}\sqrt{\frac{RT}{M}} \cdot \frac{1}{\tau_n - \tau_0} \log_e \frac{a_0}{a_n} \qquad . \qquad . \qquad (3)$$

Thus if τ_0 and τ_n, a_0 and a_n are observed, p can be calculated.

A correction should be made for the damping due to the fibre. If λ' is the decrement at the lowest attainable pressure, then in equation (3), instead of $\dfrac{1}{\tau_n - \tau_0} \log_e \dfrac{a_0}{a_n}$, $\lambda - \lambda'$ should be used, where λ is got from (2).

A long time after Kundt and Warburg's experiments, Sutherland[1] suggested a gauge based on this principle. Subsequently Hogg[2] and then Shaw[3] showed that it is possible in this way to measure pressures above 0.35μ. But the instrument is not suitable for practical use.

(b) *Knudsen's Experiments.* Knudsen has written two papers on the oscillation of a body suspended *in vacuo* by means of a torsion fibre ; he was not trying to make a pressure

[1] W. Sutherland, *Phil. Mag.*, 43, 83, 1897.

[2] Hogg, *Proc. Am. Acad.*, 42, 115, 1906.

[3] Shaw, *Proc. Phys. Soc. Lond.*, 29, 171, 1917.

gauge, but his investigations have a very important bearing on the working of viscosity gauges.

The first of these papers[1] was on the determination of molecular weights with small quantities of gases and vapours. In equation (3), if p is known, M can be calculated. So that Knudsen's work showed that the pressure indicated by a viscosity manometer is inversely proportional to the square root of the molecular weight of the gas.

The coefficient A in equation (1) is proportional to the ratio $\dfrac{\eta}{L}$, which depends only on the average velocity of the molecules and on the density; the latter is equal to the product of the number of molecules per unit volume and the mass of one molecule. So that, for a gas at very low pressure, it should be possible to obtain an equation similar to (1), but in which η does not appear, since η has no precise physical meaning when the molecules experience no collisions, but pass directly from one surface to the other. Knudsen has shown that, if N is the number of molecules per unit volume at a pressure p, m the mass of 1 molecule and Ω the average velocity of the molecules, the total mass which strikes 1 sq. cm. of the surface in 1 second is

$$\tfrac{1}{4}Nm\Omega$$

or, substituting

$$\frac{1}{4}\frac{M}{R}\frac{p}{T}\sqrt{\frac{8}{3\pi}}\sqrt{\frac{3RT}{M}}=\sqrt{\frac{M}{2\pi RT}}\cdot p.$$

Suppose that, as regards the rate of change of momentum tangentially, the accommodation coefficient is unity—that is, that the molecules are caught on the surface for a finite interval of time, such that they assume the velocity of the surface and are then given off at random according to Maxwell's Law. If the velocity of the moving surface is 1 cm. per sec., the expression given above will give the loss of momentum of the boundary per sq. cm. per sec. Thus the force B will be given by

$$B=p\sqrt{\frac{M}{2\pi RT}} \qquad . \qquad . \qquad . \qquad (1')$$

[1] M. Knudsen, *Ann. d. Phys.*, 44, 525–530, 1914.

which is very similar to equation (1), but it does not contain a. Knudsen applied this equation to the motion of a hollow glass sphere concentric with a second sphere. If the damping couple acting on a sphere oscillating about a diameter is $\Gamma\dfrac{da}{dt}$, then

$$\Gamma\frac{da}{dt} = 2\int_0^{\frac{\pi}{2}} B \cdot 2\pi r \cdot r\cos\theta \cdot d\theta \cdot r\cos\theta \cdot \frac{da}{dt} \cdot r\cos\theta \,.$$

$$= \frac{8}{3}\pi B r^4 \frac{da}{dt},$$

and if I is the moment of inertia of the sphere and λ the logarithmic decrement,

$$\lambda = \frac{8\pi B r^4}{3} \cdot \frac{1}{2I}.$$

Substituting for B,

$$\lambda = \frac{2}{3}\frac{r^4}{I} p\sqrt{\frac{2\pi M}{RT}}.$$

In his experiments Knudsen determined the variation of λ with p. The advantage of this method is that the damping of the suspension can then be eliminated from the calculation of M. The couple produced by the damping of the suspension is added on to that due to the gas. The differential coefficient of the observed decrement is equal to that of the decrement due to the gas alone. Thus if $\dfrac{d\lambda}{dp}$ is the observed value of the rate of change of λ with p, then

$$\frac{2r^4}{3I}\sqrt{\frac{2\pi M}{RT}} = \frac{d\lambda}{dp}$$

and therefore

$$M = \frac{9RT}{8\pi} \cdot \frac{I^2}{r^8} \cdot \left(\frac{d\lambda}{dp}\right)^2 \qquad . \qquad . \qquad . \qquad (4)$$

Knudsen's apparatus is shown in fig. 54. The suspended sphere A, blown as perfectly as possible (minimum diameter 3·426 cm., maximum 3·444 cm.), was graduated in half-degrees at its equator. It was placed (the author does not

say how) inside another sphere concentric with it, and the distance between the two was about 5 mm. A rod of platinum iridium was fused in as an axis, and this rod carried a silver wire E which was used to balance the sphere, so that the graduations on the sphere kept in the field of the microscope F when the sphere oscillated. A small piece of iron was fixed on in order to enable oscillations to be set up. The suspension was a quartz fibre 18 cm. long and $25 \cdot 2\mu$ in diameter. The moment of inertia of the oscillating
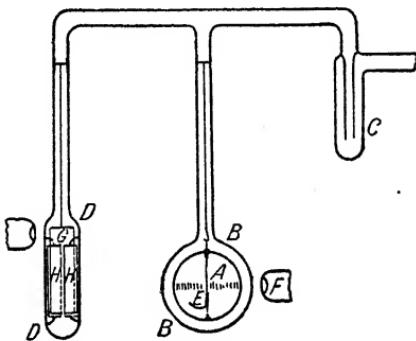
FIG. 54.

system was $6 \cdot 159$ grm. $\times$ cm.^{2}. The amplitudes were read to one-twentieth of a degree. This apparatus was connected to a radiometer gauge, and through a liquid air trap C to a molecular pump and to a system of pipettes, in order to introduce known quantities of gas.

A set of six determinations of the decrement in oxygen under pressures between 0·06 and 3·489 microbars gave a constant value for $\dfrac{d\lambda}{dp}$. This quantity diminishes when the pressure rises above 3·5 microbars; this shows that the mean free path then ceases to be large compared with the distance between the spheres. Substituting in equation (4) for

$$R = 83 \cdot 15 \times 10^6, \ T = 290 \cdot 7°\text{A.}, \ I = 6 \cdot 159, \ r = 1 \cdot 717,$$

and

$$\frac{d\lambda}{dp} = 84 \cdot 8 \times 10^{-6}$$

the value of M is 31·6, instead of 32—an error of about 1·25 per cent.

This result seems to verify the assumption of the value unity for the accommodation coefficient as regards tangential motion. But this is only verified for one gas. Experiments with saturated water vapour at −75° C. gave 21·1 instead of 18 for M.

In some later work, Knudsen [1] tried to verify the truth of the assumption made above, and also tried to get experimental evidence about the thermal accommodation coefficient

$$\alpha = \frac{E_1 - E_2}{E'_1 - E_2}$$

where E_2 is the kinetic energy of the molecules before striking the boundary, E_1 the energy after, and E'_1 the energy they would have if they came into temperature equilibrium with the boundary. Some values of this coefficient have already been quoted. In some earlier work, Knudsen [2] found the following values for polished platinum :—

	H_2	O_2	CO_2	He	A	Ne
$\alpha=$	0·278	0·800	0·807	0·338	0·857	0·653.

Now if the energy in the above equation is taken as the energy of translation alone, then

$$\alpha = \frac{c_1{}^2 - c_2{}^2}{c'_1{}^2 - c_2{}^2},$$

c_2 and c_1 being the velocities before and after impact, and c'_1 the average velocity corresponding to the temperature of the solid boundary. Consider an element dS of a boundary which is moving as shown in fig. 55, with a velocity v making an angle x_1 with the normal. Suppose that the temperature is uniform throughout the enclosure and the boundaries. Let Ω be the average velocity corresponding to this temperature. Knudsen put

$$c'_1 = \Omega$$
$$c_2 = \Omega + v \cos z$$

[1] M. Knudsen, *Ann. d. Phys.*, 46, 641–656, 1915.
[2] M. Knudsen, *Ann. d. Phys.*, 34, 593, 1911.

and therefore

$$c_1 = \Omega\left[1 + \frac{v}{\Omega}(1-a)\cos z\right].$$

Starting from this point, Knudsen gets the following expression for the value of the resistance per sq. cm. of a surface of area S moving with a velocity v,

$$B = \tfrac{1}{4}Nmv\Omega\int[1 + 2{\cdot}778(1-0745a_1)\cos^2 x_1]dS$$

where N and m have their usual significations. Neither the
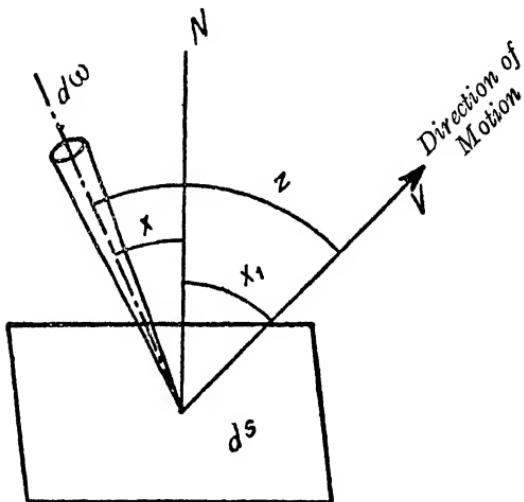
FIG. 55.

degree of approximation nor the exact method of arriving at this result is made clear in the paper.

From this expression it follows that for tangential motion $\left[x_1 = \dfrac{\pi}{2}\right]$, B is independent of a. This is not true for normal motion ($x_1 = 0$).

The following experiments were undertaken by the author to test the foregoing results. Two thin plates of polished German silver, 20 cm. long, 1 cm. wide, and 0·03 cm. thick, were suspended *in vacuo* from quartz fibres, so that one vibrated tangentially and the other normally about its 1 cm.

axis. The bars were set into motion at the same time. The ratio between the resistances to motion of the two is given by

$$y = 3.778(1 - 0.055a).$$

y was got directly by measuring the decrements, and the following results were obtained :—

with H_2 $y_{obs.} = 3.66$ $y_{calc.} = 3.72$ for $a = 0.28$
,, O_2 $y_{obs.} = 3.48$ $y_{calc.} = 3.61$ for $a = 0.80$

Thus for a gas at pressures lower than 1 microbar the resistance to normal motion of a plane is three and a half times the resistance to tangential motion. These results seem to show that the accommodation coefficients are physical realities and can be used for calculating momentum exchanges. In spite of this, the rather roundabout methods of getting these results leave still some room for doubt.

(c) *Langmuir and Dushman's Molecular Gauge.* In Kundt and Warburg's method the viscous forces are measured by the damping between an oscillating disc on a torsion fibre and a fixed parallel disc. Obviously the drag can also be measured by rotating the disc which was formerly fixed and measuring the angle of twist of the fibre supporting the other disc. This arrangement has often been used for measuring the viscosity of gases. Langmuir[1] proposed its use in measuring very low pressures, and Dushman[2] made a model for this purpose.

The rotating disc A (fig. 56) is of thin aluminium, and is attached to a shaft H, carrying a magnetic needle NS. The glass container penetrates inside a Gramme ring, supplied at six points with current from a commutating device rotated by a motor. In this way the speed of the disc can be varied from a few revolutions per minute up to 10,000.

The disc C is of very thin mica. A small mirror M is attached to the mica disc by a framework of thin aluminium. When the disc A is in position, C is laid on top of it, and the glass tube is pulled out at the top, or a suitable piece is joined on there. A small hole is made at the top and the quartz

[1] I. Langmuir, *Phys. Rev.*, 1, 337, 1913.
[2] *Phys. Rev.*, 5, 212, 1915.

fibre is threaded through, and the mirror hook is caught up on the fibre. The distance between the discs is then settled, and the fibre is fixed in position by joining a short piece of platinum to the glass bead on the quartz fibre and then fusing in the platinum with a little glaze.

If C is the torsion couple per unit angular twist, r the radius
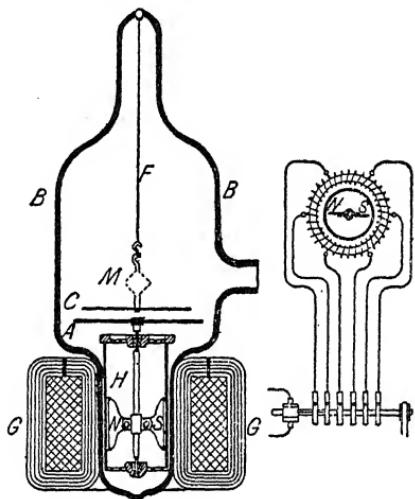
FIG. 56.

of the suspended disc, and ω the angular velocity, then, from equation (1) in § 6 (a), we have

$$C\alpha = \int_0^r A p \omega r . 2\pi r . dr . r \sqrt{\frac{M}{RT}} = \frac{\pi r^4}{2} A p \omega \sqrt{\frac{M}{RT}}.$$

If θ is the period of oscillation of the disc, and I its moment of inertia, then

$$\theta = 2\pi \sqrt{\frac{I}{C}}$$

and

$$\alpha = \frac{r^4 \theta^2}{8\pi I} A p \omega \sqrt{\frac{M}{RT}}.$$

In one of Dushman's models the weight of the disc was only 0·1 gram. ; its radius was 2 cm., and its time period 24 secs. ; then for this disc $I = \frac{1}{2} \times 0·1 \times 4 = 0·2$.

For 1000 revs. per minute $\omega = \dfrac{1000 \times 2\pi}{60}$.

And if Knudsen's hypothesis is true $A = \dfrac{1}{\sqrt{2\pi}}$ (equation 1′, § 6 (b)). Under these conditions, for nitrogen at a pressure of 1 microbar at 300° A.,

$$a = 147°.$$

Thus the pressure corresponding to a deflection of 1 mm. on a scale 50 cm. away would be

$$p = \frac{1}{2} \times \frac{1}{500} \cdot \frac{180}{\pi} \cdot \frac{1}{147} = 0 \cdot 4 \times 10^{-3} \text{ microbars.}$$

So that it would be possible, theoretically, to measure to 10^{-4} microbars by increasing the speed to 10,000 revs. per minute.

But for such low pressures serious difficulties arise. Although the amount of metal in the suspended system is cut down as far as possible, the deviations due to Foucault currents are greater at very low pressures than those due to the gas. Thus one of Dushman's models gave a deviation of 525 mm. for a pressure of 1 microbar, when the speed was 1000 revs. per minute, so that for 10^{-3} microbars with 10,000 revs. per minute the deflection should have been 5·25 mm. But the deviation found was between 25 and 30 mm. For the lowest pressures which can be got with a molecular pump and a liquid air trap the deviation obtained was only 1 or 2 mm. greater than that due to Foucault currents. This is the result deducible from the calibration measurements with much higher pressures and speeds at which the Foucault currents are negligible. The calibration determines the sensitivity S and the value of the constant K in the formula

$$a = Sp\omega + Ki^2\omega$$

where i is the current in the Gramme ring.

There is also a tendency for the upper disc to start swinging, especially for high speeds of rotation of the aluminium disc.

As might be expected, the results show that the proportionality of the deflection to the pressure, and to the number of

revolutions per minute, is only true when the distance between the discs is small compared with the mean free path of the molecules. Since this distance is in practice of the order of 5 mm., the limit of proportionality between deflections and pressures will be at about 20 microbars.

The author has shown that the deflection is approximately proportional to the square root of the molecular weight of the gas.

To sum up, this apparatus seems to be useful for studying the properties of gases at low pressures, but of very little value as a pressure gauge for ordinary use. Dushman himself came to this conclusion.

7. **The Quartz Fibre Gauge.** As a last example of pressure gauge we shall describe briefly a very simple arrangement which is calibrated purely by comparison, but is often very useful. The method consists of setting a quartz fibre into vibration and measuring the damping. This increases with the pressure.

Langmuir [1] used this method for observing the changes in pressure in a sealed-off incandescent lamp whilst the lamp was in use. The quartz fibre was fixed inside the bulb. When the lamp (a tungsten filament lamp) had just been lit (initial pressure $0·018\mu$), it took 66 minutes for the amplitude to drop to half the original value. After 3 hours' running at 2 watts per candle-power, it took 175 minutes. Thus the residual gases were gradually disappearing. This action will be discussed in Chapter IV. The long time taken for a measurement shows that the arrangement is only suitable in special cases.

Haber and Kerschbaum [2] used this device for measuring the vapour pressures of mercury and iodine. They give an empirical formula for the relation between the time t to fall to half amplitude and the partial pressures of the different vapours present. This formula can be written

$$\Sigma(p\sqrt{M}) + a = \frac{b}{t},$$

[1] I. Langmuir, *J. Amer. Chem. Soc.*, **35**, 107, 1913.

[2] *Zeits. f. Electrochem.*, **20**, 296, 1914.

when a and b are constants, p is the partial pressure of one of the vapours, and M its molecular weight. They were able to measure pressures down to 0·015 microbar in this way. From work done at the General Electric Co.'s laboratory it would seem that it can be used for much lower pressures than this.

8. **Conclusions.** The McLeod gauge is still the standard instrument for the practical measurement of low pressures. Nevertheless its accuracy is quite uncertain below 0·1μ. Moreover; it is only suitable for permanent gases, and its readings can be completely wrong if small traces of easily condensable vapours are present. In practice the mercury vapour from the gauge causes no inconvenience, because the liquid air trap which is necessary to get rid of condensable vapours will also take up the mercury vapour.

For pressures lower than 0·1μ several manometers, of the molecular type and the ionisation type, have been tried. The ionisation gauge is attractive because of its rapidity of reading and its sensitivity ; but the phenomena called into play are more complex than those in molecular gauges, and these have scarcely been sufficiently investigated up to the present. Knudsen's gold leaf manometer seems to be the most practicable; and the Pirani gauge is also a handy instrument.

Theoretically the indications of Knudsen's absolute manometer are independent of the nature of the gas, which makes this instrument superior to all the others. But this is only true for Knudsen's original model, and we have not yet got an absolute manometer which is really suitable in practice. The radiometer gauges approximate to absolute manometers at very low pressures. But experiment alone tells us just at what pressure the nature of the gas comes in, so that the radiometer gauges, although sometimes styled absolute manometers, must be calibrated either by comparison with a McLeod gauge at suitable pressures, or by introducing known volumes of gas at known pressures, as described above. A separate calibration should be made for each gas. Thus the accurate measurement of low pressures is closely bound up with the microanalysis of gases.

CHAPTER III

CONNECTING TUBES. THE ELIMINATION OF OCCLUDED
GASES. LEAKS. THE MICROANALYSIS OF GASES

1. **Conductance of a Tube.** When only Toepler pumps and
similar devices were available for reaching low pressures, the
diameters of the tubes used did not matter very much. The
output of these pumps was so small that the pressure was
practically the same throughout the whole tube system at
any time. Put more exactly, this means that the pressure
difference between the vacuum chamber and the pump
which was necessary to produce the flow of an amount
of gas equal to the output of the pump was practically
negligible.

With the Gaede rotary mercury pump this was no longer
true for the diameters and lengths of connecting tubes which
were formerly used. With molecular pumps, condensation
pumps, and even the latest oil pumps with high speeds, it
has become absolutely necessary to select connecting tubes
of such diameters and lengths as are suited to the output of
the pump, if the latter is going to be used to the best
advantage.

The problem may be stated in the following way : Suppose
a vacuum chamber of volume V is joined to the pump by a
cylindrical tube of diameter D and length l, how will the
pressui e in the vacuum chamber vary with the time ? If the
pressure in the pump is kept at p, how long will it take for the
pressure x in the vacuum chamber to reach a value which
differs from p by some fixed fraction ? This problem is
obviously of the greatest importance also in the correct
interpretation of manometer readings.

Let us take for granted at present that all parts of the tube system are at the same temperature.

Let P be the mean pressure of the gas in the tube, and U_1 the product of this pressure, and the volume of the gas, measured at the pressure P, which would flow from the tube into the pump under a driving pressure difference of 1 microbar. If the driving pressure difference is $x-p$, the output of the tube per second will be $U_1(x-p)$, and in time dt it will be $U_1(x-p)dt$.

Applying Boyle's Law,

$$U_1(x-p)dt = -dV \cdot x = -Vdx \qquad . \qquad . \qquad (1)$$

In his first paper,[1] Knudsen gave the following expression for the conductance of a tube :—

$$U_1 = \frac{\pi D^4 P}{128\eta l} + \frac{1}{6}\sqrt{2\pi} \cdot \frac{1}{\sqrt{\rho_1}} \cdot \frac{D^3}{l} \frac{1 + \frac{\sqrt{\rho_1}}{\eta}PD}{1 + 1 \cdot 24\frac{\sqrt{\rho_1}}{\eta}PD} \qquad . \qquad (2)$$

where η is the viscosity of the gas and ρ_1 its density under a pressure of 1 microbar.

Since P is the mean pressure, we can put

$$P = \frac{x+p}{2} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

These equations will obviously give a differential equation which will allow us to calculate x as a function of t, if p is known in terms of t and x (the initial pressure in the vacuum chamber).

The first term in equation (2) corresponds to Poiseuille's Law for the flow of a fluid through a cylindrical tube, which is followed in the case of a gas when the diameter of the tube is large compared with the mean free path. The fraction at the end of the second term corresponds to the transition stage between purely viscous flow and the state of flow reached when the mean free path becomes large compared with the diameter of the tube. When the mean pressure P is very

[1] M. Knudsen, *Ann. d. Phys.*, **28**, 75–130, 1909.

small this fraction becomes unity, and the expression assumes the simple form

$$U_1 = \frac{1}{6}\sqrt{2\pi}\frac{D^3}{\sqrt{\rho_1}.l} \qquad . \qquad . \qquad . \qquad (4)$$

Knudsen showed that the values calculated from this equation were never more than 5 per cent. out, even when D was equal to $0.4L$, where L is the mean free path, so that, if equation (4) is to apply, we must have

$$\frac{D}{L} < \cdot 0.4.$$

If L_0 is the mean free path at a pressure of 1 bar (about 750 mm. Hg.), we can put

$$\frac{DP}{L_0 \times 10^6} < 0.4 \quad \text{or} \quad DP < 4 \times 10^5 L_0.$$

The following table gives the values of L_0 for some of the common gases :—

	Air.	H$_2$.	He.	N$_2$.	O$_2$.	A.	CO$_2$.	CO.	NH$_3$.
$L_0 \times 10^6$ cm. at 1 bar and 20° C.	9·376	17·44	27·45	9·287	9·931	9·879	6·148	9·232	6·60

So that the limiting diameters, if equation (4) is to apply, are :

	Air.	H$_2$.	He.	N$_2$.	O$_2$.	A.	CO$_2$.	CO.	NH$_3$.
$D<$	mm. 37·5	mm. 69	mm. 110	mm. 37·2	mm. 39·7	mm. 39·5	mm. 24·6	mm. 36·9	mm. 26·4

So that for all gases, with tubes of ordinary diameters, equation (4) applies when the mean pressure is 1 microbar. It would still apply up to 5μ or even 10μ with the tubes which

were commonly used with Toepler or Geissler pumps, and with tubes such as are generally used in work on gases.

If equation (4) applies we can calculate P as a function of the time by combining it with equation (1). Let x_0 be the pressure at the vacuum chamber end of the tube when $t=0$, and let the temperature be $T°$ Abs., and M the molecular weight of the gas,

$$U_1 = \frac{\sqrt{2\pi} \cdot D^3}{6\sqrt{\rho_1} \cdot l} = \frac{\sqrt{2\pi}}{6}\sqrt{\frac{10^6 \times 22708}{M}} \cdot \sqrt{\frac{T}{273}} \cdot \frac{D^3}{l}$$

$$= \frac{62 \cdot 8 \times 10^3}{\sqrt{M}} \sqrt{\frac{T}{273}} \cdot \frac{D^3}{l} \qquad (5)$$

and

$$-U_1 dt = \frac{V dx}{x - p}.$$

And since U_1 is independent of the mean pressure, and therefore independent of x,

$$\log_e \frac{x - p}{x_0 - p} = -\frac{U_1}{V}t$$

or

$$x - p = (x_0 - p)e^{-\frac{U_1 t}{V}} \qquad . \qquad . \qquad . \qquad (6)$$

Let us take an example.   Suppose

$p = 0.1$ microbar, $x_0 = 10$ microbars, $D = 0.3$ cm., $l = 100$ cm., $V = 1000$ c.c.,

and that the gas is nitrogen at 0° C. Let us calculate how long it will take for the pressure in the vacuum chamber to fall to twice the value of the pressure at the other end of the tube, that is 0.2 microbar.

$$\frac{x_0 - p}{x - p} = \frac{10 - 0.1}{0.2 - 0.1} = 100 \text{ approx.}$$

Substituting in (6)

$$t = \frac{V}{U_1} 2 \cdot 303 \cdot \log_{10} \frac{x_0 - p}{x - p} = \frac{V\sqrt{M}}{62 \cdot 8 \times 10^3} \frac{l}{D^3} \times 2 \cdot 303 \times 2 = 1440 \text{ secs.}$$

Thus, under these conditions, with a pump having a big enough output and low enough limiting pressure to keep the pump end of the tube at 0·1 microbar, it will take 24 minutes for the pressure in the 1-litre vacuum chamber to get down to twice the pressure at the other end of the connecting tube. It would take one and a half times as long to get down to eleven-tenths of the pressure at the pump end [since $\dfrac{(x_0 - p)}{(x - p)} = 1000$], that is 36 minutes, and after 48 minutes the vacuum chamber pressure would only be 1 per cent. higher than that at the pump end of the tube.

If there is a pressure gauge at the pump end of the connecting tube, we can get the pressure in the vacuum chamber from its readings only if we know the unit output U_1 of the connecting tube.

Equations (5) and (6) also show the disadvantage of narrow bore taps. The effect of a tap of bore diameter D' and length of bore l' on a tube of diameter D will be equivalent to adding a length l to the latter, such that

$$\frac{l}{D^3} = \frac{l'}{D'^3} \quad \text{or} \quad l = l' \frac{D^3}{D'^3}.$$

Suppose $D = 1$ cm., $D' = 0·1$ cm., and $l' = 1$ cm., $l = 1000$ cm., or 10 metres. This shows that it is not much good cutting down the lengths of the connecting tubes as far as possible if narrow bore taps are fitted between the tubes. Only big taps with at least 3 mm. bore should be used in vacuum tube systems, and even then, with a length of bore 10 mm., this corresponds to 37 cm. of 10 mm. tubing.

Let us now examine the case of the McLeod gauge to find out how long it takes for equalisation of pressure between the bulb and the fine bore capillary and compression chamber. It seems possible, considering the example given above, that the equalisation might be quite slow.

Let V be the volume of the bulb, and kV that of the compression chamber, l be the length of the capillary, and D its diameter. Let p be the pressure in the bulb. To make a measurement the mercury level is brought to the upper

graduation, and, when this is done, the pressure in the compression chamber will be x_0, say $= \dfrac{p}{k}$. Suppose the mercury is lowered so rapidly that we can neglect the time of this operation, so that at $t=0$ the pressure in the top of the capillary is x_0, and P in the bulb.

Suppose x_0 changes to x in time t. Although there is mercury vapour present, let us apply equation (6). We get

$$\log_e \frac{\dfrac{p}{k} - p}{x - p} = \frac{U_1}{kV} t.$$

Let us calculate the time taken for $x - p$ to reach a fixed fraction of p, say ϵp,

$$t = \frac{kV\sqrt{M}}{62 \cdot 8 \cdot 10^3} \cdot \frac{l}{D^3} \cdot 2 \cdot 303 \log_{10} \frac{1}{k\epsilon}.$$

Let us take $V = 250$, $k = 10^{-5}$, $l = 10$, $D = 0 \cdot 08$, which correspond to a gauge with minimum compression chamber 5 mm. long, and a sensitivity of $0 \cdot 01\mu$ for 1 mm. difference of level. Suppose that the capillary is 25 cm. long (the range of the gauge will then be from $0 \cdot 01\mu$ to 50μ). Take $M = 28$ and $\epsilon = 0 \cdot 01$, we get

$$t = \frac{10^{-5} \times 250\sqrt{28} \times 10 \times 2 \cdot 303 \times 7}{62 \cdot 8 \times 10^3 \times 8^3 \times 10^{-6}} = 0 \cdot 067 \text{ sec.},$$

so that the equalisation is practically instantaneous in spite of the small diameter of the capillary. This is due to the very small volume of the compression chamber. The calculation is only very approximate, because the gas diffuses into mercury vapour, and also because Knudsen's Law cannot apply to the beginning of the flow on account of the high pressure then obtaining in the compression chamber (1 mm. of mercury). At this pressure the maximum value of the diameter for the application of Knudsen's Law would be $0 \cdot 037$ mm. ($0 \cdot 4$ times the mean free path).

2. **Influence of Connecting Tubes on the Speed of a Pump.** Suppose that a tube of length l and diameter D is used to

join a pump to a vacuum chamber.   Let x be the pressure in
the vacuum chamber and p that in the pump at the same
instant.   Let dv_2 be the volume of gas leaving the vacuum
chamber in time dt, dv_2 being measured at the pressure x; and
let dv_1 be the volume entering the pump in the same time,
measured at p.   Equation (I) can be rewritten in the form

$$U_1(x-p)dt = xdv_2 = pdv_1.$$

If S_1 is the actual speed of the pump according to Gaede's
definition, and S_2 its apparent speed, measured by the varia-
tion of pressure in the vacuum chamber, then

$$S_1 = \frac{dv_1}{dt}, \quad S_2 = \frac{dv_2}{dt},$$

so that

$$U_1(x-p) = xS_2 = pS_1.$$

$$\frac{1}{S_2} = \frac{1}{S_1} + \frac{1}{U_1} \qquad . \qquad . \qquad . \qquad (7)$$

By using this equation we can find the loss of speed of rapid
pumps like molecular pumps or condensation pumps when
they are joined to tubes which are too narrow.   Take, for
example, a pump with a speed 2000 c.c. per sec. at a
pressure of 10 microbars, joined to a vacuum chamber (or a
pressure gauge) by a tube 10 cm. long and 1 cm. in diameter.
Taking $T = 273°$ Abs., and substituting in (5)

$$U_1 = 1070,$$

and in (7)

$$\frac{1}{S_2} = \frac{1}{2000} + \frac{1}{1070}$$

$$S_2 = 700 \text{ c.c. per sec.}$$

Thus the pump has only 35 per cent. of the speed it would
have if it were joined to a very short and wide tube.   With
a tube 2 cm. in diameter the speed would be 1620 c.c. per sec. ;
for 3 cm. diameter it would reach 1900 c.c. per sec.   For tubes
1 metre long instead of 10 cm. the speeds would be 102, 800,
and 1270.

Thus, in order to get the best out of a pump which has a

very low limiting pressure and a big output, it must be joined to the vacuum apparatus by tubes which are as short and wide as possible. The diameters should be at least 2 cm. If this is not done the speed, even with molecular pumps or condensation pumps, will be no greater than that of the earlier pumps, such as the Gaede rotary mercury pump.

The above also shows how difficult it is to measure the real speed of a pump. It is practically impossible with a McLeod gauge, the result being always too low.

3. **Flow through a Hole in a Thin Plate.** It is sometimes necessary to know the amount of gas flowing through a hole in a thin plate when the diameter of the hole is small compared with the mean free path of the gas molecules. The calculation is simple. Let N_0 and N be the numbers of molecules per unit volume on the two sides of the hole, and let p_0 and p, ρ_0 and ρ be the corresponding pressures and densities. Let m be the mass of a molecule and let Ω be the average velocity. The mass which passes through per sq. cm. per sec. is equal to the difference between the masses which cross both ways, and is therefore given by

$$\mu = \frac{1}{4}N_0 m\Omega - \frac{1}{4}Nm\Omega = \frac{1}{4}\Omega(\rho_0 - \rho).$$

But

$$\rho_0 = \frac{M}{RT}p_0 \qquad \rho = \frac{M}{RT}p \qquad \Omega = \sqrt{\frac{8}{3\pi}}\sqrt{\frac{3RT}{M}} = \sqrt{\frac{8RT}{\pi M}},$$

so that

$$\mu = (p_0 - p)\sqrt{\frac{M}{2\pi RT}}.$$

If we define the output as the product of the mean pressure P_m and the volume flowing through per second measured at P_m, and if A is the area of the hole, then

$$u = \mu A \frac{P_m}{\rho_m} = \mu A \frac{RT}{M} = (p_0 - p)\sqrt{\frac{RT}{2\pi M}} A,$$

and if ρ_1 is the density at 1 microbar

$$u = (p_0 - p)\frac{A}{\sqrt{2\pi\rho_1}}.$$

The unit output u_1, corresponding to a driving pressure difference of 1 microbar, will be given by

$$u_1 = \frac{A}{\sqrt{2\pi\rho_1}} = \frac{60 \cdot 10^3}{\sqrt{M}} \sqrt{\frac{T}{273}} A \quad . \quad . \quad (8)$$

4. **The "Resistance" of a Tube.** Equation (1) may be written in the form

$$-\frac{d(Vx)}{dt} = U_1(x - p).$$

The left-hand side can be looked upon as the output of a gas of unit density under unit driving pressure; and $x - p$ is the driving pressure. Thus $\frac{1}{U_1}$ can be looked upon as a resistance : that is, the resistance of the tube against the driving pressure for a given output. The resistance of a cylindrical tube, if the flow is in accordance with Knudsen's Law, is given by

$$W_1 = \frac{1}{U_1} = 1 \cdot 59 \times 10^{-5} \sqrt{M} \sqrt{\frac{273}{T}} \cdot \frac{l}{D^3} \quad . \quad (9)$$

and for a circular hole

$$w_1 = \frac{1}{u_1} = 2 \cdot 12 \times 10^{-5} \sqrt{M} \sqrt{\frac{273}{T}} \cdot \frac{1}{D^2} \quad . \quad (10)$$

In order to follow up the analogy with Ohm's Law some writers on this subject calculate the resistance instead of the output. It must be remembered that the current intensity is replaced by the rate of change of the product-pressure multiplied by volume. To get the mass of the output this quantity should be multiplied by the density under unit pressure at the temperature T.

5. **Influence of a Temperature Difference between Two Parts of a Tube. Thermal Transpiration.** Suppose that a porous plug is fixed in a tube and a temperature difference is established between the two ends. Experiment shows that gas will flow through the plug from the cold to the warm side. If the ends of the tube are sealed the equilibrium pressure will be higher on the warm side as long as the temperature difference persists.

This may be shown in a striking manner by placing a little electric heater inside a porous tube, and closing the latter at one end and joining the other end to a manometer or a delivery tube. The inner wall of the porous tube will be warmer than the outside, so that air flows in, and the pressure difference may amount to several centimetres of mercury, or, in the case of the delivery tube, the output may be 100 c.c. per minute.

This phenomenon was first observed by Neumann,[1] and then by Feddersen.[2] They thought it was due to absorption. Osborne Reynolds[3] and Maxwell[4] showed that it was in accordance with the kinetic theory of gases. Reynolds investigated the phenomenon with plugs of plaster of Paris and meerschaum ; he found that if T_1 and T_2 are the absolute temperatures of the faces of the plug, then the equilibrium pressures on the two sides are related by the equation

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \ . \qquad . \qquad . \qquad . \qquad (11)$$

Maxwell worked out the case for a tube with a uniform temperature gradient established along it, without a porous plug. He calculated the pressure gradient $\frac{dp}{dt}$, in the case where the diameter of the tube was large compared with the mean free path.

These papers were lost sight of until Knudsen[5] began to study the phenomenon. Equation (11) is often attributed to him, although he has himself pointed out the mistake. It is obvious that thermal transpiration must be taken into account in measuring pressures in tube systems which are unequally heated. This often happens when parts of the system are heated to drive off surface gases.

Let V_1 and V_2 (fig. 57) be two vacuum chambers joined

[1] C. Neumann, *Ber. d. Königl. Sächs. Gesell. d. Wissensch. Math. Phys.*, **24**, 9, 1872.

[2] Feddersen, *Pogg. Ann.*, **148**, 302, 1873.

[3] Osborne Reynolds, *Phil. Trans.*, p. 127, 1879.

[4] Clerk Maxwell, *Phil. Trans.*, p. 231, 1879.

[5] M. Knudsen, *Ann. d. Phys.*, **31**, 205–229 and 633–680, 1910.

by a tube.   For the sake of simplicity let us suppose that
there is a discontinuity of temperature at a section A of
the connecting tube, so that the temperature in the chamber
V_1 and in the tube up to A is T_1, and T_2 from A to V_2 and
throughout V_2.   Let m be the mass of 1 molecule of gas, N_1
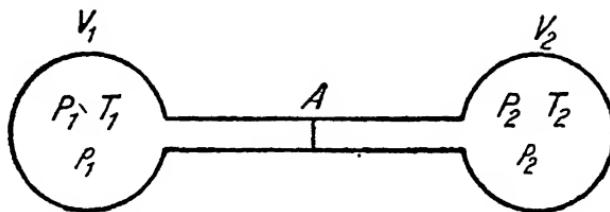
FIG. 57.

and N_2 the numbers per c.c. in V_1 and V_2, and Ω_1 and Ω_2 the
average velocities corresponding to T_1 and T_2.   The values
of the pressures are given by

$$p_1 = \frac{\pi}{8} N_1 m \Omega_1^2, \qquad p_2 = \frac{\pi}{8} N_2 m \Omega^2.$$

If the condition for equilibrium is got by equating these
pressures, then if ρ_1 and ρ_2 are the densities,

$$\frac{\rho_1}{\rho_2} = \frac{N_1 m}{N_2 m} = \frac{\Omega_2^2}{\Omega_1^2} = \frac{T_2}{T_1}.$$

But equilibrium is not established by equalisation of
pressure, but from the equality of the amounts of matter
which travel from left to right, and from right to left in one
second across the section A.   Experiment shows that when
the diameter of the tube is large compared with the mean
free path (at atmospheric pressure, for example) there are
two currents.   The outer layers of gas move from the cold
to the warm end, and the more central layers move in the
opposite direction, as shown in fig. 58.   The equilibrium
condition is then the equality of the mean pressures on both
sides of A.   But when the diameter is small compared with
the mean free path, there can be no " fluid " flow of layers
of gas, because the number of collisions between molecules is
small compared with the number of impacts on the tube wall.

In this case the number of molecules crossing 1 sq. cm. in one second is $\frac{1}{4} N\Omega$. Thus, for equality of numbers of molecules crossing A in opposite directions,

$$N_1\Omega_1 = N_2\Omega_2,$$

so that

$$\frac{p_1}{p_2} = \frac{N_1 m\Omega_1{}^2}{N_2 m\Omega_2{}^2} = \frac{\Omega_1}{\Omega_2} = \sqrt{\frac{T_1}{T_2}}$$

and

$$\frac{\rho_1}{\rho_2} = \frac{N_1 m}{N_2 m} = \frac{\Omega_2}{\Omega_1} = \sqrt{\frac{T_2}{T_1}}.$$

The essential phenomenon in this case is what Knudsen calls molecular flow—that is, there is no motion correspond-

Cold   Hot
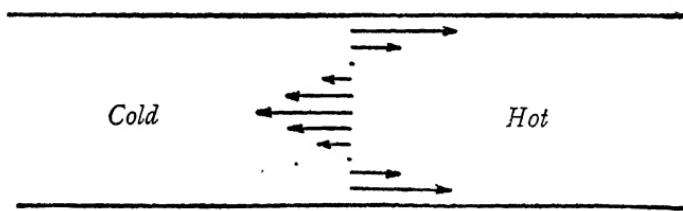
FIG. 58.

ing to the flow of liquids. The above results can be extended to the case of a continuous temperature variation along a length of the tube connecting the two vacuum chambers. The pressure at any point is always given by $p = \frac{\pi}{8} N m\Omega^2$.

Then the quantity $\frac{1}{4} N m\Omega$ may be taken as constant along the tube, because it gives the mass of gas impinging per second on 1 sq. cm. of the walls of the tube; thus the pressure at any point will be proportional to the average velocity Ω and, therefore, proportional to the square root of the absolute temperature at this point.

Thus equation (11) only applies at low pressures or to very fine capillaries. If the pressure is high enough, so that the mean free path is small compared with the diameter of the tube, without, however, the double current described above

being negligible (as is the case at atmospheric pressures), then either Maxwell's or Kundsen's equation may be used for the pressure gradient. These equations are not very different. Knudsen's form is

$$\frac{dp}{dT} = \frac{0 \cdot 00139 \, \dfrac{1 + \dfrac{C}{273}}{1 + \dfrac{C}{T}} \, \dfrac{\eta_0}{\sqrt{\rho_0}} \, k_1}{R + 25 \cdot 98 \, \dfrac{\sqrt{\rho_0}}{\eta_0} \cdot \dfrac{1 + \dfrac{C}{T}}{1 + \dfrac{C}{273}} \, R^2 \cdot \dfrac{p}{T}} \qquad . \qquad (12)$$

R is the radius of the tube, η_0 the viscosity at $0°$ C., ρ_0 the density at $0°$ C. under a pressure of 1 microbar, C is Sutherland's constant, and k_1 is a coefficient whose value depends on the form of the isothermal surfaces in the tube. This coefficient is unity when these surfaces are planes perpendicular to the axis of the tube, which is the case for fine tubes or low pressures. In all cases k_1 is less than $\frac{4}{3}$.

According to Knudsen, equation (12) does not apply to pressures which are intermediate between those for which R is small compared with the mean free path and those for which R is very large compared with the mean free path. Equation (12) depends on the supposition that the molecules which strike an element of bounding surface have speeds corresponding to the temperature of the surface. For pressures which are intermediate in the sense defined above this cannot be true, since the molecules reaching the surface come from points which are far enough from the surface to have velocities corresponding to temperatures differing from the surface temperature at the point of impact. For this case Knudsen gives the following equation :—

$$\frac{dp}{p} = \frac{3}{8} k \frac{1}{1 + \dfrac{2R}{\lambda}} \frac{dT}{T} \qquad . \qquad . \qquad . \qquad (13)$$

where λ is the mean free path given by

$$\lambda = \frac{1 \cdot 12 \sqrt{\pi}}{\sqrt{8} \times 273 \times 0 \cdot 3097} \cdot \frac{\eta_0}{\sqrt{\rho_0}} \cdot \frac{T}{p}$$

and k is a numerical coefficient which varies slowly with the ratio $\dfrac{2R}{\lambda}$ and tends to the value $\dfrac{4}{3}$ when $\dfrac{2R}{\lambda}$ tends to 0. In this limiting case the equation reduces to

$$\frac{dp}{p} = \frac{1}{2} \frac{dT}{T},$$

which corresponds to equation (11).

It will be seen that the equations are much simpler at
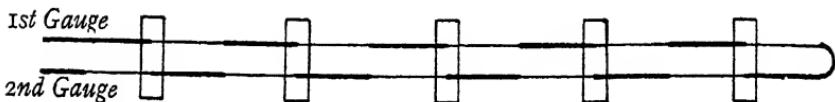
FIG. 59.

low pressures than at high pressures, and that the equation is very complicated for intermediate pressures.

From the point of view of vacuum work, equation (11) is the interesting case. No rigorous experimental verification of this equation seems to have been attempted. Knudsen's work related to the verification of equations (12) and (13), and cannot be regarded as entirely satisfactory. His arrangement is shown in fig. 59. Two McLeod gauges were joined together by a tube 10·2 mm. in diameter joined through 10 capillary lengths 0·374 mm. in diameter; corresponding joints were heated to 500° C. by means of wire wound on asbestos paper. The results given on p. 139 were obtained for hydrogen. The pressures are given in millimetres of mercury.

It will be seen from the table that the pressure in the first gauge, which is joined to the warm joint, may reach ten times that in the second gauge, which is joined to the cold joint. The ratio $\dfrac{p_1}{p_2}$ passes through a maximum.

p_1.	p_2.	p_1-p_2.	$\dfrac{p_1}{p_2}$(obs.).	$\dfrac{p_1}{p_2}$ (calculated from (12)).	
				$k_1=1$.	$k_1=1\cdot45$.
mm.	mm.	mm.			
0·00978	0·00419	0·00559	2·33		
0·278	0·0314	0·247	8·85		
0·475	0·0476	0·427	9·98		
3·601	1·169	2·432	3·09	2·153	3·303
4·834	2·058	2·776	2·35	1·917	2·906
16·5	15·1	1·4	1·09	0·96	1·22
65·2	64·8	0·4	1·006	0·33	0·50
235·1	235·0	0·1	1·0005	0·06	0·14
760·0	No observable pressure difference.				

In another set of experiments Knudsen used a porous plug of magnesia pressed in between two end plugs of asbestos. The diameter of the containing tube was 7·5 mm., and the length of the magnesia plugging 7·6 cm. Two gauges were joined to the ends of the tube. One end of the plug was raised to 250° C. and the other kept at 22° C. It is interesting to notice the slowness of establishment of equilibrium conditions, and also the pressure differences reached. The gas used was hydrogen. p_1 and p_2 are the pressures indicated by the gauges, in millimetres Hg : t is the time.

t.	p_1.	p_2.	p_1-p_2.
	mm.	mm.	mm.
0	0·3000	0·3000	0
$18^h\,25^m$	0·3308	0·2716	0·0592
$23^h\,25^m$	0·3347	0·2693	0·0654
$46^h\,50^m$	0·3414	0·2641	0·0774
∞	0·3428	0·2628	0·0800
	mm.	mm.	mm.
0	3·871	3·871	0
$24^h\,5^m$	4·239	3·527	0·712
$48^h\,10^m$	4·325	3·451	0·874
$71·15^m$	4·341	3·428	0·913
∞	4·346	3·424	0·922

These results agree fairly well with equation (13).   If k is put equal to $\dfrac{4}{3}$ in (13), we get

$$\frac{p'_1}{p_2}=\left(\sqrt{\frac{T_1}{T_2}}\right)^{\frac{1}{1+\frac{2R}{\lambda}}} \qquad . \qquad . \qquad . \qquad (14)$$

when p'_1 is the pressure at the first warm joint, and is equal to p_1 (the pressure at the first gauge) plus the rise of pressure p'', corresponding to the fall in temperature between the warm joint and the gauge, these being joined by the 7·5 mm. tube.   The value of this correction is calculated from equation (12).   For the first set of experiments :

$$p''=0\cdot0040 \qquad (p'_1)_\infty =0\cdot3468 \qquad \frac{p'_1}{p_2}=1\cdot320 \qquad \sqrt{\frac{T_1}{T_2}}=1\cdot329.$$

For the second set :

$$p''=0\cdot001 \qquad (p'_1)_\infty =4\cdot347 \qquad \frac{p'_1}{p_2}=1\cdot271 \qquad \sqrt{\frac{T_1}{T_2}}=1\cdot323.$$

Thus in the first set of experiments, for very low pressures, if $\dfrac{2R}{\lambda}$ is put $=0$ in equation (14), which then assumes the form of equation (11), the results agree well with the theory. In the second set the mean free path must be taken into account, and to do this the value of R must be known. R is the radius of the capillary tube which is equivalent to the interstices between the particles of magnesia.   The value of R is determined by applying equation (14) to the second set of results and calculating the value of $\dfrac{2R}{\lambda}$, and therefore R, for agreement with this equation.   The values obtained are

$$\frac{2R}{\lambda}=0\cdot168, \ \lambda=0\cdot0040 \text{ cm., and therefore } R=0\cdot00068 \text{ cm.}$$

Now if this value of R is substituted in (14) for the first set of results, we get

$$\left(\sqrt{\frac{T_1}{T_2}}\right)^{\frac{1}{1+\frac{2R}{\lambda}}}=1\cdot318 \quad \text{and} \quad \frac{p'_1}{p_2}=1\cdot320,$$

which shows satisfactory agreement and thus justifies the use of equation (11) for very low pressures.

Thus equation (11) enables us to calculate the true pressure and density in a vacuum chamber from the gauge reading, if we wish to know these. In many cases, however, the only use of the gauge is to show that the low-pressure limit has been reached. Let us take a numerical example to show the order of the correction. Suppose that the gauge is at 288 Abs. and the vacuum chamber is at 773 Abs.; and let p_1 and ρ_1 be pressure and density in the vacuum chamber, and p_2 and ρ_2 those in the gauge,

$$p_1 = p_2 \sqrt{\frac{773}{288}} = 1 \cdot 64, \qquad \rho_1 = \rho_2 \sqrt{\frac{288}{773}} = 0 \cdot 61.$$

The total mass of gas in a tube system in which the pressures are low is given by

$$m = \left(v_1 \sqrt{\frac{T_0}{T_1}} + v_2 \sqrt{\frac{T_0}{T_2}} + \dots\right)\rho_0 . \qquad . \quad (15)$$

where v_1, v_2, etc., are volumes of parts of the system at temperatures T_1, T_2, etc., respectively, T_0 is the temperature in the gauge, and ρ_0 the density of the gas at T_0 and p_0, where p_0 is the pressure given by the gauge.

6. **The Construction of a Tube System.** For vacuum apparatus the whole system, vacuum chambers, gauges, connecting tubes, and pumps, should be joined up, as far as possible, by fused glass joints and metal joints fused on to glass (platinum, tungsten, and special alloys), for the following reasons :—

1. It is very much quicker to fuse together two glass tubes, even wide ones (20 to 25 mm.), than to make a good waxed joint.

2. Waxed and ground joints prevent the tubes from being heated sufficiently to drive off surface gases, this being absolutely necessary if very low pressures are to be reached (except in special cases).[1]

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[1] The exceptional circumstances referred to are the waxed or ground joints used with metal condensation pumps. These joints are not as bad as similar joints in the middle of the tube system, because the gases which come off from the surfaces near the joints are quickly taken out of the low-pressure part of the system, owing to the high speed of the pumps. In spite of this action it is better to use pumps made with Pyrex glass, which can be fused on to the tube system.

3. Leaks are very easily detected in an all-glass apparatus by a method described further on. This method will not work with waxed joints. It is also much easier to spot a small crack in glass than in wax.

4. The pressure of the vapour from wax is quite appreciable, even at temperatures at which the wax is quite hard.

Thus waxed or ground joints must only be used when they cannot be avoided. Ground joints with grease must be used if one tube has to be rotated, and waxed joints for glass and metal. Details are given further on of methods of fusing together glass and metals, but in practice waxed joints are more usual.

Vacuum Waxes. Golaz wax has been in use since Regnault's time. It is made of 3 parts of resin, 1 part of beeswax, 1 part of tallow, and about 4 parts of fine mineral powder. Many waxes of this kind are on the market.

Waxes of this kind melt rather too easily and too completely. In America a different kind of wax is used, the basic material being gum lac. Waxes of this type are more plastic and more elastic than the Golaz type. When they are heated they soften until they are something like india-rubber, instead of flowing. This makes it rather harder to get the wax on to the joints, but these will then stand fairly high temperatures. They also stand well up to cold, which is very useful. Often a joint will hold up for months, and then, owing to a change of atmospheric temperature or some other accidental cause, it will crack imperceptibly and cause a great deal of trouble, especially if the crack is small and invisible. Surface melting does not always cover the leak.

Many American workers use what is called Khotinski cement. It is made by macerating gum lac in 10 per cent. of its weight of " North Carolina Oil of Tar " in a water bath. The wax is heated until mixture is complete and it has the desired consistency. A similar and cheaper wax can be made by heating gum lac with from 5 per cent. to 10 per cent. of anthracene oil from the gasworks. This oil is got by distilling coal tar and collecting only the products which come over at above 300° C. When it is cooled the anthracene crystallises

out.   The liquid left over is used with the gum lac, which it dissolves when heated.

No systematic study seems to have been made of the vapour tension and the mechanical properties of the different waxes and cements used in vacuum work.   This work would be of great practical value in improving the preparations and constitution of these waxes, which have often rather low melting-points and begin to give off very appreciable amounts of vapour at fairly low temperatures (about 60° C.).   These
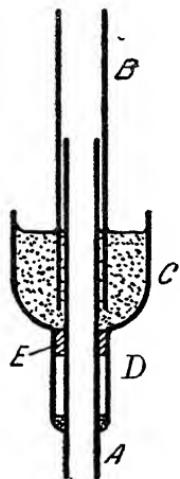

Fig. 60.

waxes would no doubt be improved by prolonged heating *in vacuo* to remove the more volatile constituents.

It is usual to join two tubes together by wrapping some warm wax round the smaller tube and then slipping the larger tube into the wax ring, so that the larger tube slides over the smaller, and the wax completely covers the end of the larger tube.   A better joint can be made by the following process :   *A* and *B* are the two tubes (they may be in different glasses which will not fuse together).   A cup *C* is threaded on to the end of *A* (the smaller tube).   The cup is fused on to *D*, which is a few centimetres long, and a little wider than *A*. *E* is a strip of asbestos paper which holds *C* and *D* in position. A little molten wax is poured into *C*, and then *B* is slipped

in round A with the end of B about half-way down the wax. B should be warmed before this is done.   Joints made in this way do not crack as easily as the ordinary bulbous joints, and they are much easier to take apart and remake than the latter.   The above process should always be used for a joint on wide tubing.   McLennan always used this method for his ultra-violet spectrograph.   One of the ends for joining is used as a horizontal reservoir, into which the warm wax is poured, and the other end is then warmed and slid into the wax.   The tubes must not be heated too much, or the wax will boil and become porous and brittle and fill the tube system with troublesome vapour.

Plastic varnishes with cellulose as basic material, which are used for enamelling wire and in aeroplane wing-making, are quite useful.   As a rule these varnishes contain a cellulose ether, a solvent, and some substance which gives plastic properties.   When they are dried in air and then baked slowly they become very hard, stand up to heat very well, and have a very low vapour pressure.   The following tests which I carried out indicate their properties.   An enamel of this type, which was slightly viscous when cold, was used to fill in the meshes of a piece of wire gauze soldered on to the end of a tube (the tube was 30 mm. in diameter, and the gauze about 25 meshes to the square cm.).   After drying for two or three hours the enamel was baked for three hours at from 60° C. to 100° C.   The pressure in the tube was kept down as low as 1μ at a temperature of 150° C.   At this temperature one of the meshes blew in.   A ground joint without grease, if covered with a thin layer of this enamel and suitably baked, will keep tight down to 1μ up to temperatures at which the enamel is quite liquid.   Enamel of this kind can also be used to cover a crack in glass, and will completely stop the leak. If the glass tube does not need to be warmed much the enamel need not be baked.   It can be allowed to dry until it will not stick to the fingers, and then the hardening started by blowing warm air over it.

From the point of view of hardness, standing up to heat, and low vapour pressure, bakelites (condensed phenols), used like the enamels above, might be better than the cellulose

materials. Unfortunately, it is very difficult to get them to stick to glass or metal. It must be noted that cellulose enamels, even when well baked, flake off under water, which gets under the edge of the enamel.

In sealing off the constriction in a capillary with a blowpipe the following rule should be observed. First the part should be heated as strongly as possible without melting for some minutes, with the pumps still running. The melting and sealing is then done quickly. This precaution gets rid of the gas which comes off during the heating of the glass. The following results, due to Dushman (*loc. cit.*), show this very well. An ionisation gauge of 100 c.c. capacity was evacuated down to 0·001 microbar and then sealed off without the above precautions being taken. After sealing the pressure rose to 0·25 microbar. When the constriction was heated before sealing the pressure only rose to 0·01 microbar.

Fused Joints between Metals and Glass. These joints are very important in all pieces of apparatus into which electrodes must be led. If the apparatus is of ordinary glass the conductor passes in through a bead of blue glass, which fuses easily on to glass and to platinum, and also to some alloys of iron and nickel. These alloys are in general use in the electric-lamp industry, and are called " platinite " and " platinor." Platinite is a white alloy containing 54 per cent. of iron (with 0·15 per cent. of carbon) and 46 per cent. of nickel. Its mean coefficient of expansion is $7·5 \times 10^{-6}$, which is about the same as that of blue glass. The wire sold under the name of " platinor " looks just like copper. The metal is nearly all iron and nickel, covered with a thin coating of copper, which is again coated with a borax preparation, which gives it a slightly bluish tint. Platinite often gives gas bubbles which are held in the bead of blue glass. The joints with platinor are better looking and more solid. However, it is difficult to get the blue glass to stick round platinor wires which are over a millimetre in diameter. With platinite, and still more with platinor, the wire itself must not be heated directly with a flame. The wire is threaded into a capillary, which is then melted on to it. For wires of big diameter platinum joints are much better than those with

ferro-nickel (perhaps because the platinum surface does not oxidise, and so sticks to the glass better).

It is much easier to get glass to stick round a tube of platinum than round a solid wire or rod. This is probably due to the fact that the thin tube can shrink more easily with the glass, and because, for a thick wire, it is hard to get the cooling at the outer surface of the glass bead equal to that at the metal glass surface. Some years ago [1] I was able in this
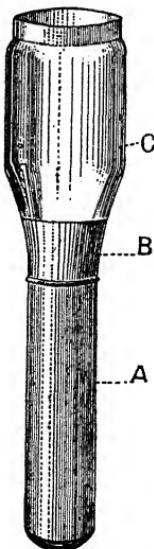

FIG. 61.

way to fuse into glass platinum tubes from 5 to 6 mm. in diameter, and also a circular plate about 0·3 mm. thick and 25 mm. in diameter.

Some recent work by Housekeeper [2] in the laboratory of the Western Electric Co. also shows that the use of thin tubes makes the sealing of metals through glass much easier. He has succeeded in sealing glass tubes 90 mm. in diameter into copper tubes. The ends of the copper tubes are bevelled. Fig. 61 shows the arrangement.

[1] L. Dunoyer, *Ann. d. Phys.*, **27**, 519, 1912.
[2] W. Wilson, *Electrical Communication*, pp. 15–21, Aug. 1922; Housekeeper, *Amer. Inst. Elec. Eng.*, **42**, 954, 1923.

With joints of this kind it is possible to make thermionic valves with an output of even 1000 k.v.a. The idea underlying the process is that, by suitably varying the thickness of glass and metal, it is possible to arrange that the forces produced by temperature variations at the joint do not exceed the elastic limit of the glass.

Quite good joints of this kind can be made by an electrolytic process first suggested by Cailletet. The end of the glass tube is first covered outside, when warm, with a thin film of bright platinum. This is done with a fine emulsion of platinum chloride in an essential oil, such as clove oil or camomile oil. The oily liquid is spread on the glass and heated gently to a dull red. The difficulty is to get an even film of platinum, since it often separates out in drops and leaves parts of the glass bare. Copper is deposited electrolytically on the platinum, and a metal tube can be soldered on to the copper in the ordinary way. The soldering can be dispensed with by covering the line of the joint with an electrolytic deposit. To do this the line must be as fine as possible. This is arranged by grinding the glass into the metal tube, which has a bevelled end, as shown in fig. 62. The metal tube is slipped into a short copper tube which serves as the anode, and the electrolyte is poured into this.

Joints of this type have been described by McKelvy and Taylor,[1] and also by Meyers.

When Pyrex glass is used the current leads are made of molybdenum or of tungsten, which fuse easily into Pyrex, even in rings of large diameter. The metal is heated until it is white hot before it is slipped into the capillary tube, which is melted on to it. Unless this is done there will be a large number of bubbles in the glass at the joint. Another glass made by the Corning Glass Works (G–702–P) fuses easily to tungsten. This same firm produces two intermediate glasses which enable platinum to be fused into fused quartz, and enable quartz to be joined to Pyrex.

Taps, Mercury Cut-offs, and Traps for Condensable Gases. It has already been mentioned that, except in special cases,

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[1] McKelvy and Taylor, *J. Amer. Chem. Soc.*, 42, 1364, 1920; C. H. Meyers, *ibid.*, 45, 2135, 1923.

the taps used in vacuum work should be as big as possible. Most of the taps usually sold are far too small. The big taps are usually sold at excessive prices compared with the small ones, but they are no harder to make and the cost of the extra material is negligible. All taps used in a tube system should have inclined bores, so that gas cannot leak straight

Platinised Glass (*cathode*)

Copper anode

Metal (*cathode*)
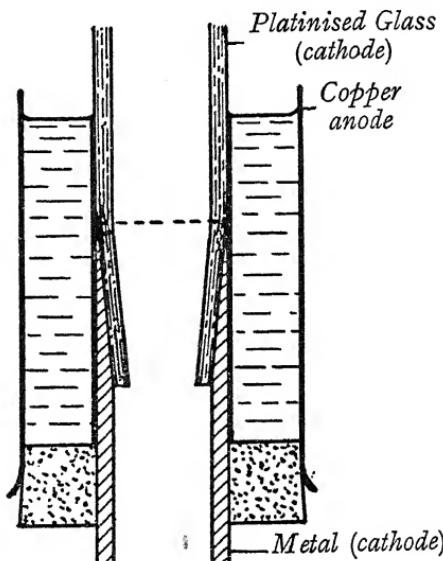
FIG. 62.

round, following the streaks in the tap grease. It is always difficult to avoid these streaks.

The choice of tap grease is important. It should give off very little vapour and should never stick. The best tap grease is made by dissolving pure non-vulcanised Para rubber in white vaseline and in paraffin. This is best done in a water bath. The amount of rubber is gradually increased, until the grease forms threads when it is pressed between the fingers. About 1 part of white vaseline, 1 part of paraffin, and 2 parts of rubber will do. The grease is filtered and then kept *in vacuo* for at least twenty-four hours, warmed up to about 40° C.

This grease gives off very little vapour when it is kept cool, and it is easily possible to get down to 0.1μ or 0.01μ

when it is used. If the greased joint is near the pump and the latter has a big output, it is possible to get even lower. But in many cases it is better to get rid of grease altogether. This is the great advantage of the glass condensation pump over the metal pump. The taps are replaced by mercury cut-offs like those shown in fig. 63. As a matter of fact these
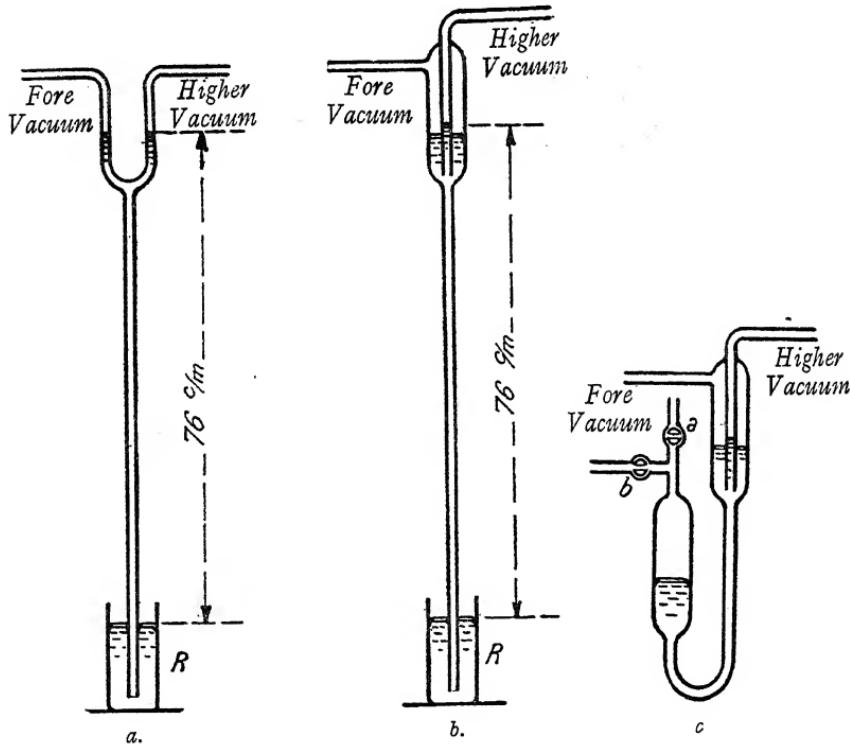

FIG. 63.

cut-offs are only useful to separate two parts of the system between which the pressure difference is small, as, for example, between the fore vacuum and the high vacuum ; but a tap can always be put in on the fore vacuum side. The cut-off should be arranged so that R can be raised or lowered a few centimetres. The size of the cut-off can be diminished by using the shape shown in fig. 63, c. If the tap a is closed and b opened to the high vacuum, the cut-off opens ; in order to close it b is closed and a little atmospheric air is let in through

a. These cut-offs have been used in all the work done under Langmuir and under Campbell on incandescent lamps and valves. In researches of this kind not only must all grease be got rid of, but also mercury vapour and all condensable vapours (traces of water vapour, etc.). To do this traps like that shown in fig. 64 are used, so that a part of the tube system through which the gases must pass can be kept at a low temperature. Either liquid air or a mixture of carbon dioxide snow and acetone are placed in the Dewar vessel.
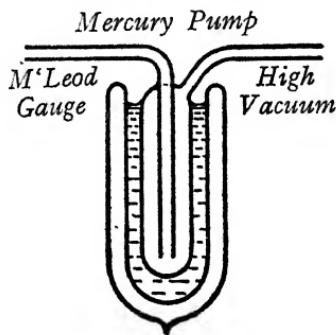

FIG. 64.

Dushman has measured the vapour pressures at low temperatures of gases usually occurring in vacuum tubes (*loc. cit.*). His results are given on p. 151.

The usual sources of low temperature in laboratories are liquid air and carbon dioxide snow. Using these, a series of baths at fixed temperatures can be got by freezing liquids of known composition. As examples there are melting mercury ($-39°$ C.), melting chloroform ($-65°$ C.), melting acetone ($-95°$ C.), melting ethyl alcohol ($-117°$ C.), carbon dioxide snow subliming under atmospheric pressure ($-78°$ C.), boiling oxygen under atmospheric pressure ($-183°$ C.), and boiling nitrogen under atmospheric pressure ($-196°$ C.). The temperature of liquid air is not constant; when it is fresh, its temperature is $-190°$ C. under atmospheric pressure ; but nitrogen evaporates quickest, and after a few hours the liquid becomes richer and richer in oxygen and the temperature rises towards $-185°$ C. If it is not necessary to reach any definite temperature, but only to condense the vapours

	Hg.								
Temp. °C.	$+30°$	$+20°$	$+10°$	$0°$	$-10°$	$-20°$	$-40°$	$-78°$	$-180°$
Vap. press. in microbars.	3·7	1·6	0·65	0·25	0·087	0·029	0·0023	$4·3 \times 10^{-6}$	$2·3 \times 10^{-24}$

	$H_2O.$								
Temp. °C.	$-20°$	$-30°$	$-40°$	$-50°$	$-60°$	$-75°$	$-89°$	$-100°$	$-110°$
Vap. press. in microbars.	1045	380	127	39	9·6	1·0	0·1	0·01	0·001

	$CO_2.$				$C_2H_4.$				$C_2H_6.$			
Temp. °C.	$-148°$	$-168°$	$-182°$	$-193°$	$-175·7°$	$-188°$	$-197°$	$-205°$	$-150°$	$-180°$	$-190°$	$-198°$
Vap. press. in microbars.	100	1	0·91	0·0001	1013	101·3	10·13	1·013	10,130	101·3	10·3	1·013

	$CH_4.$			A.		$O_2.$		CO.		$N_2.$	
Temp. °C.	$-164·7°$	$-185·8°$	$-201·5°$	$-186·2°$	$-194·2°$	$-182·9°$	$-211·2°$	$-190°$	$-200°$	$-195·8°$	$-210·5°$
Vap. press. in mm. Hg.	760	79·8	50·2	760	300	760	7·75	760	249	760	86

present, either carbon dioxide snow in acetone ($-78°$ about) or liquid air is used. Dushman's figures lead to the following conclusions :—

1. Carbon dioxide snow gets rid of practically all the mercury vapour present. (However, experiments on glow potential show that in general the elimination is not complete, at any rate after some hours.)

2. Carbon dioxide snow will not get rid of water vapour, since the pressure of the latter is only lowered to the

low pressure limit of the best pumps by cooling well below $-100°$ C. Thus if liquid air is not available a phosphorous pentoxide bulb must be put in to get rid of water vapour. Experiment shows that water vapour is taken out as completely with solid carbon dioxide and P_2O_5 as it is with liquid air, but the action is much slower.

3. The pump itself will take out the carbon dioxide. But the limiting pressure is reached much sooner if a liquid air trap is used.

4. The vapour pressures of the light hydrocarbons (ethylene, ethane, and methane) are still appreciable at $-200°$ C.

The results also show that, in order to freeze out mercury vapour, water vapour, and carbon dioxide, the trap should not be cooled until the other less easily condensable gases have been taken out by the pump. If there are traces of light hydrocarbons in the condensed vapours, pressures below the saturation pressures of the condensed gases are only reached after a long time.

Hardly any data are published about the vapour pressures of oils suitable for oil pumps. According to Dushman they are of the order of 1 microbar at ordinary temperature, 0·1 microbar at 0° C., and quite negligible at the temperature of solid carbon dioxide. The rubber grease described above has a vapour pressure certainly lower than this, so that it can be used with molecular pumps or metal condensation pumps so long as a carbon dioxide snow trap is also used.

It should also be noted that a mercury trap should always be placed between a condensation pump and an oil fore vacuum pump to protect the latter from the mercury. It is obviously needless to use a low temperature trap. Cold water will do, or even a bulb surrounded by the air. The bulb should be filled with little bits of glass to increase the condensation surface.

Detection of Leaks. It is much easier to find a leak in an all-glass apparatus than in metal tubing or metal pumps. In the latter case it is always a difficult and long business, and sometimes it is impossible to find the leak at all.

In a glass apparatus the best way is to use a little induction coil giving a spark of about 7 or 8 mm. One end of the

secondary is joined to any metal part [1] with a surface inside the tubes. The other end of the secondary is joined to a wire with rubber insulation. The pressure in the apparatus is lowered to from 50 to 200μ, and then the free end of the secondary is carried by hand nearly touching the tubes. It is better to make a little brush of wire at this end to cover a greater surface. The tubes glow and a brush discharge, visible in the dark, goes on between the free end of the secondary and the surface of the tube. When this end gets near the hole the brush discharge changes to a bright spark discharge between the gas inside and the brush, through the tiny hole. Very fine holes can be detected in this way, even if they are fine enough to let the pump get down to 1μ or even lower, depending, of course, on the pump and on the dimensions of the apparatus. If the output of the pump is big these fine holes are very troublesome, since they may be in some apparatus which is going to be sealed off. The only sure way is to make careful measurements of the limiting pressure ; even if this seems high this may be put down to the slow liberation of occluded gases. Once the hole is found it is easy to close it with a little drop of glass, using a blowpipe. The method is so easy that it is a good thing to make a rule of using it every time a tube system is set up or a new piece added on. The limit to the use of the method is that it will only work when the length of the hole is less than the length of the spark in air ; and the spark length cannot be made too long owing to the risk of piercing the glass tubing when the wall is thin. Thus, it cannot be used, as a rule, round ground joints or waxed joints. Of course, it will not work for glass-metal joints, or even near these joints.

For metal parts, the best way is to immerse them in water and blow air into them, as is usually done for rubber tyres. Very fine holes can be detected in this way. If the apparatus cannot be put in water it can be painted with soapy water. With fairly big holes bubbles are quickly formed, but with tiny holes the method is not very good, since there are always

[1] If there should be no such part, a little tinfoil stuck on a tube will do.

small bubbles due to the roughness of surfaces, and because the film dries before the bubble has time to grow.

If there is a discharge tube of any kind in the apparatus, leaks can easily be detected with petrol. The tube system is pumped out until a rose-coloured air discharge takes place, and then petrol is painted over the apparatus with a small brush. When the petrol gets to the leak the discharge turns grey. This method is useful for waxed joints, and the petrol will often soften the wax sufficiently to close a small crack.

To stop a leak in metal apparatus it is sometimes convenient to varnish it with one of the cellulose varnishes described above (in the section on vacuum waxes). The pressure in the apparatus should be atmospheric before the varnish is applied. The varnish can be hardened *in situ* by blowing warm air over it (a hair-dryer is very convenient for this).

Rubber Tubing. Rubber is not used very often in apparatus which is destined for high vacuum work. Rubber tubing is, however, very convenient for joining on to fore vacuum pumps and molecular pumps, and it is also in very common use in McLeod gauges. In the latter case the air trap between the mercury reservoir and the measured bulb gets rid of any gas from the rubber. The rubber used should have the lowest possible sulphur content. The gas emission from it is also very much cut down by boiling it for several hours in caustic soda solution and then in distilled water, and finally drying it with a current of dust-free air. By following this treatment Holweck found that a molecular pump easily got away any liberated gas from the rubber, and enabled him to reach very low pressures. The length of tubing should be cut down as far as possible.

The gas from rubber contains a large proportion of hydrogen, both free and combined, and it gives the Balmer series quite brilliantly under discharge. A small piece of rubber introduced into an evacuated tube, which is then sealed off, makes quite a good Geissler tube for the hydrogen spectrum, although of course other lines are present.

Rubber tubing tends to become porous in time. This can

be avoided by coating it externally with castor oil. It is also a good thing to coat the joints between rubber and glass and rubber and metal. In a good many lamp factories the lamps are attached to the vacuum apparatus by sticking the sealing-off tubes of the lamps into rubber bungs, and applying castor oil.

7. **Elimination of Occluded Gases from Glass and Metals.** When a glass vessel is pumped out with a pump with a low limiting pressure and a big output, the layer of water which always sticks to glass surfaces begins to evaporate very rapidly. After a few minutes the rate of evaporation slows down a good deal, and it is often possible to get the pressure down to 1 microbar, and sometimes even to 0·01 microbar. But if the vessel is then sealed off from the pump, the pressure gradually rises, owing to the slow liberation of surface gases, of which water vapour forms a large part. This emission takes place at room temperature. The following is an example of this: A 9-litre vessel was evacuated down to 1 microbar and sealed off. In ten hours the pressure rose to 95 microbars, about a hundred times the initial value. The emission is quickened by heating the vessel. This is the reason why Crooke's tubes and X-ray tubes are always heated strongly when they are being pumped out. A good deal of work has been done in order to find out the best heat treatment.

Metals also contain occluded gases and surface gases which come off during heat treatment. It is easy, for example, to get down to 0·01 microbar in a 3-litre bulb containing a tungsten filament (a large size lamp). But if, after sealing off, the filament is raised to incandescence, it gives off from three to ten times its own volume of gas (the volume of gas being measured under atmospheric pressure); since the volume of the filament is of the order of 10 cubic mm., the pressure will rise to 3·3 microbars, which is far too high for a thermionic valve.

Evolution of Gas by Heat Treatment of Glass. Influence of Temperature. It is obvious that the amount of gas given off by a sample of glass must depend on the previous history of the glass. This is probably the reason why so few figures are available from the literature of this subject, in spite of the fact

that a good deal of work has been done on it. The most definite results have been got by workers in American factory laboratories (General Electric Co., Westinghouse Research Laboratory, Western Electric, etc.). The following results are given by Langmuir in a very long paper on "The Constitution and Fundamental Properties of Solids and Liquids." [1]

A vacuum system containing a liquid air trap and the bulb for an ordinary 40-watt lamp (internal surface area about 200 sq. cm.) was pumped out as far as possible for twenty-four hours. The bulb was then raised to 200° C. for three hours. The following quantities of gas were given off :—

H_2O . . . . 200 cubic mm.
CO_2 . . . . 5 ,, ,,
N_2 . . . . 2 ,, ,,

volumes measured at room temperature and atmospheric pressure.

On raising the temperature of the bulb to 350° C., more gas was given off, and the totals were then

H_2O . . . . 300 cubic mm.
CO_2 . . . . 20 ,, ,,
N_2 . . . . 4 ,, ,,

On heating to 500° C. (this means either using Pyrex or evacuating the oven), the total quantity rose to

H_2O . . . . 450 cubic mm.
CO_2 . . . . 30 ,, ,,
N_2 . . . . 5 ,, ,,

From a knowledge of the internal surface area, and using Avogadro's number, it is possible to calculate the number of molecules coming off per sq. cm. of surface. The results are

H_2O, 56×10^{15}. CO_2, $3 \cdot 7 \times 10^{15}$. N_2, $0 \cdot 6 \times 10^{15}$.

Langmuir [2] has formulated a theory that the adsorbed gases

[1] I. Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221–2295, 1916.

[2] *Ibid.*; and 39, 1848, 1917. Langmuir has written a large number of papers dealing with this theory (see references in bibliography at the end of this book).

are held by valency bonds of chemical nature, so that they form a kind of pavement on the solid surface and constitute a unimolecular layer ; but this theory hardly seems to apply here.   The accepted values of the molecular diameters are

H_2O, $2\cdot9 \times 10^{-8}$ cm. CO_2, $3\cdot3 \times 10^{-8}$. N_2, $3\cdot15 \times 10^{-8}$.
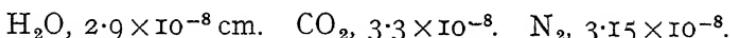
Thus, if the molecules fill in a kind of draught-board pattern, the numbers of molecules required to cover a square centimetre would be

H_2O, $1\cdot19 \times 10^{15}$. CO_2, $0\cdot92 \times 10^{15}$. N_2, $1\cdot10 \times 10^{15}$.
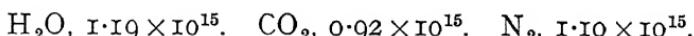
Thus the volumes quoted above correspond to a layer of H_2O molecules 47 molecules thick, a CO_2 layer 4 molecules thick, and for N_2 a layer 0·6 molecule thick.   By taking slightly different values for the molecular diameters, Langmuir gets 55, 4·8, and 0·9 instead of the above numbers.   But, even if this makes nitrogen fit the theory, the other numbers are very far out, particularly that for water.

However, the idea of a unimolecular layer is very attractive and simple, and it fits in with a large number of facts.   Therefore Langmuir supposes that the gases obtained in the vacuum experiments do not come from truly adsorbed layers, but from deeper layers.   The water, he considers, is actually dissolved in the glass.   It must also be. remembered that heat treatment *in vacuo* seems to reduce the adsorptive power of glass.

Sherwood[1] has done some more detailed work on the effect of temperature.   His results are given graphically in figs. 65, 66, 67, in which volumes of gas are plotted against temperature.   The volumes are the amounts given off during three hours' heating at the corresponding temperature.   After each heating the apparatus was evacuated as far as possible before raising to the next temperature.   *G–702–P* glass is a borosilicate of sodium and magnesium made specially for fusing in tungsten current leads ; it is rather like Pyrex, and can be fused to the latter, but not too readily.   The three sets of curves have certain common characteristics,

[1] Sherwood, *J. Amer. Chem. Soc.*, 40, 1645, 1918 ; and *Phys. Rev.*, 12, 448, 1918.

all having maxima. For total gaseous emission this is about 300° C. for G–702–P, and 150° C. for the other glasses. Above the maximum the emission of CO_2 is small, as it is also for gases which will not condense in liquid air. On the other hand, the water vapour passes through a maximum and
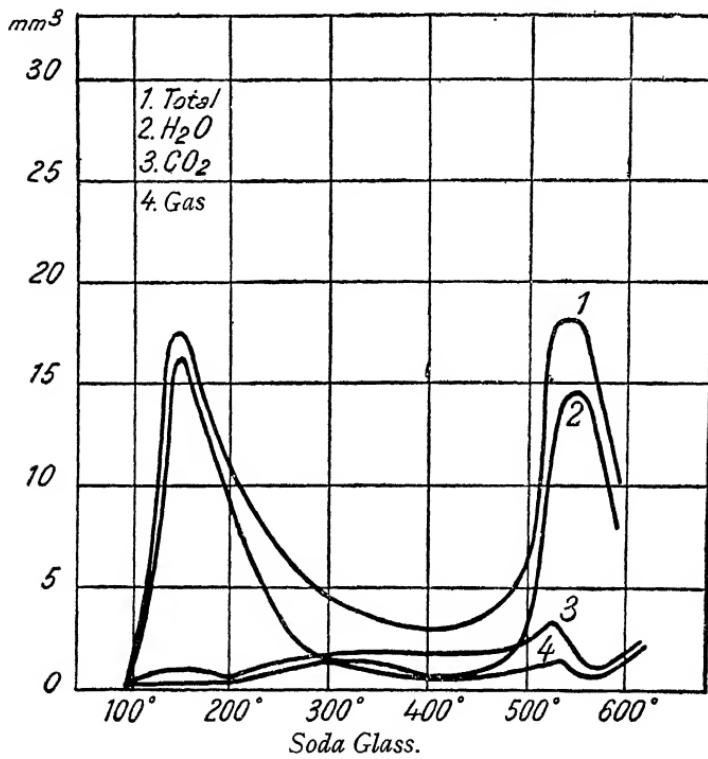

Soda Glass.
FIG. 65.

then a minimum, and then rises very rapidly when the glass begins to soften. The first maximum for soda glass corresponds to an emission of 0·15 cubic mm. per sq. cm. of surface, which corresponds to a layer 4 molecules thick. This may be considered as truly adsorbed water, whereas the large amount given off near softening probably corresponds to chemical decomposition. Thus, in order to get rid of surface gas which will come off *in vacuo*, the highest useful temperatures for heat treatment are:

Soda glass 400° C.   Lead glass 350° C. G–702–P 450°–500° C.

The following results, due to Shrader,[1] show the beneficial effects of heat treatment in vacuum practice. He used a 2-litre bulb first at room temperature, and then heated to fixed temperatures, allowing the bulb to cool to room temperature after each heating, whilst the pump was kept going.


Lead Glass.
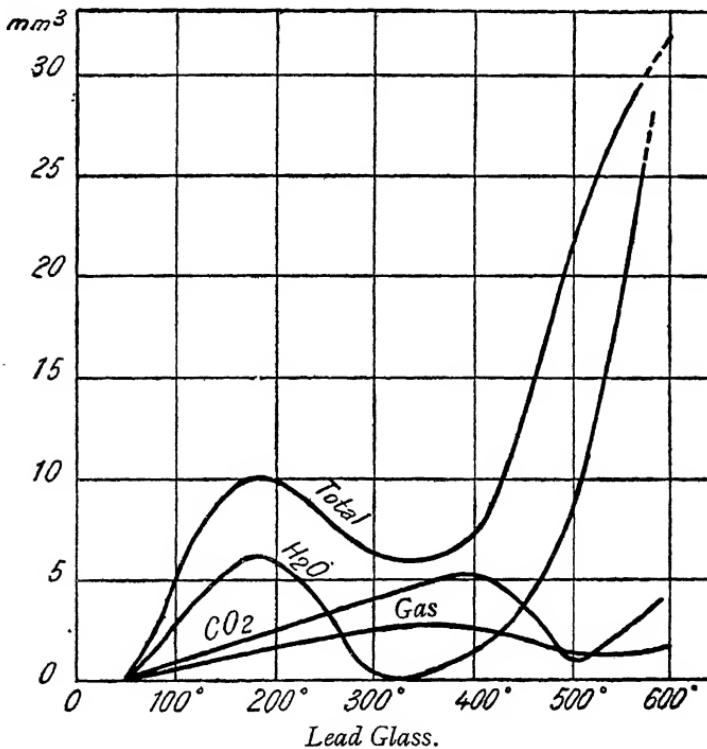
FIG. 66.

Pumping at each temperature was continued until the lowest possible pressure was obtained. The results were:

Temps.	20° C.	100° C.	200° C.	300° C.	500° C.
Pressures (microbars) }	10^{-2}	$1 \cdot 9 \times 10^{-3}$	$1 \cdot 7 \times 10^{-4}$	$1 \cdot 2 \times 10^{-4}$	$2 \cdot 4 \times 10^{-5}$

Probably the values of the pressures are not strictly dependable as absolute measures, but the proportional drop shows the great advantage of heat treatment.

[1] Shrader, *Phys. Rev.*, 13, 434, 1919.

Dushman (*loc. cit.*) also remarks that, using a Gaede rotary pump on an all-glass system which had not been heated, he could not get below 0·033 microbar ; but after heating the whole system to 330°, he got down to 0·00007 microbar (?).

Influence of Duration of Heat Treatment.   There is very


G–702–P Glass.
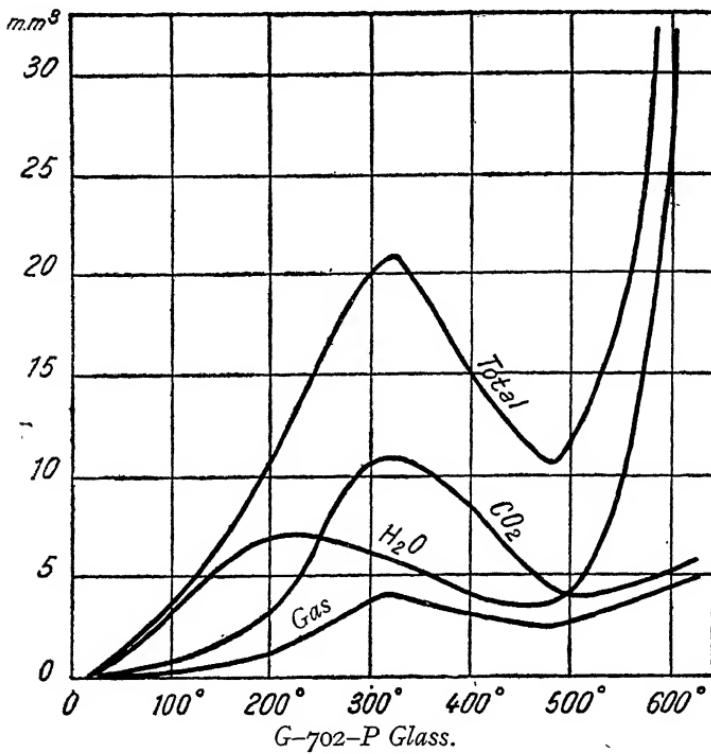
FIG. 67.

little agreement between different workers with regard to this point.   Perhaps the form of Sherwood's curves explains this.   In many of his experiments, Langmuir seems to have thought that heating for half an hour at 360° was sufficient to drive off all the gas which could come off at that temperature.   In some of his other experiments heating was continued for three or four hours.   Sherwood heated for three hours throughout.   In reality, even at temperatures lower than that at which the glass softens, three hours is not long

enough to get to equilibrium conditions. This point is very well brought out by some results given by Guichard,[1] who made a large number of experiments on the slow emission of gas from glass, porcelain, and other substances heated *in vacuo*. Thus, after seventeen hours' heating at 600° C. the gas coming off from a tube of Jena glass was sufficient to raise the pressure by 0·9 mm. per hour in a volume of 280 c.c. Emission at 600° C. stopped after forty hours' heating under a pressure of 0·01 mm.

Effect of successive Heat Treatment. The gas emission from glass is very much reduced if it is previously heated, even at atmospheric pressure. The following results, given by Langmuir,[2] illustrate this point :—

A glass bulb, which was evacuated and heated for one hour at 300° C., gave the following amounts of gas per sq. cm. : H_2O, 0·68 cubic mm. ; CO_2, 0·07 cubic mm. ; N_2, 0·07 cubic mm. A similar bulb, heated for three hours at 300° C., gave the following : H_2O, 1·3 cubic mm. ; CO_2, 0·64 cubic mm. ; N_2, 0·18 cubic mm. The amounts of water vapour correspond to molecular layers, 17 and 33 molecules thick respectively. But microscope cover glasses, bent in the flame to prevent their sticking together, and heated for one hour at 300° C. *in vacuo*, only gave the following :—H_2O, 0·18 cubic mm. ; CO_2, 0·032 ; and non-condensable gas, 0·025 cubic mm., which correspond to a 4-molecule layer of water, a 1-molecule layer of carbon dioxide, and a 0·9-molecule layer of nitrogen. Langmuir considers that these values are low, because it is difficult to make sure that the thin cover glasses are at 300°.

The gas emission from thin slips of freshly cleaved mica was less than that from the cover glasses. The slips were kept apart with little metal blocks. The total mica surface was 5750 sq. cm. After evacuation and heating to 300° for three hours, allowing for the gases from the bulb containing the slips, the following amounts were obtained per sq. cm. of surface :—H_2O, 0·086 cubic mm. ; CO_2, 0·024 cubic mm. The quantity of non-condensable gas (N_2) was negligible.

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[1] M. Guichard, *Ann. Chim.*, 6, 285, 1916.
[2] I. Langmuir, *J. Amer. Chem. Soc.*, 40, 1361, 1918.

These numbers correspond to a 2-molecule layer of water and a 0·8-molecule layer of carbon dioxide.

Mica contains about 18 per cent. of combined water. Thus the small emission at 300° C. is remarkable. According to Langmuir, mica probably cleaves along planes containing molecules of combined water, so that freshly cleaved surfaces are covered with a unimolecular layer ; but these combined molecules are part of the structure of the mica and can only with difficulty be removed by heating. When the freshly cleaved surface is brought into contact with moist air a second layer of water molecules deposits on the combined set. This second layer is not held as tightly as the first, and so is more easily removed. It would be interesting to see if the moisture really comes off in two stages when the temperature is gradually raised.

The following data, given by Langmuir,[1] also relate to the effect of heat treatment. " Three lots of lamps were made with the same structural details and operating characteristics ; the first lot was exhausted at approximately 450° C., the second lot at 550° C., and the third lot at 550° C. at first, and then at 450° C. The average life of the first lot was approximately 575 hours, that of the second lot 300 hours, and that of the third lot over 900 hours, the conditions of operation with all three lots being the same." Thus prolonged heating at the highest possible temperature is not the best heat treatment for vacuum bulbs. But a systematic study in order to find the best heat treatment does not seem to have been made up to the present.

Adsorption of Gases other than Water Vapour on Glass and Mica. According to Langmuir's results, given above, when glass is heated in a flame until it softens, it gives off a large fraction of adsorbed gases. Since all glass work is necessarily subjected to this treatment when it is made, the adsorbed gases must in part be taken from the atmosphere, and the adsorbed amounts of water, carbon dioxide, and nitrogen are much larger than the quantities which would correspond to unimolecular layers. The speed of adsorption at ordinary temperatures and atmospheric pressure has never been

[1] I. Langmuir, Patent No. 1,273,629, 23rd July 1918.

measured, but some work has been done under the direction of Langmuir on adsorption at low pressures and low temperatures.

TABLE I

ADSORPTION ON MICA AT 155° ABSOLUTE

Gas.	p microbars.	q obs. mm.^{3}/m.^{2}.	q cal. mm.^{3}/m.^{2}.	a.	b.
CO_2	172·0 98·0 41·4 20·6 11·9 7·3 4·8 3·19 2·06 1·60	96·6 86·7 77·6 61·1 46·8 36·7 29·4 24·0 16·0 10·8	93·3 88·9 77·6 63·3 50·0 38·2 28·9 21·2 15·0 12·0	0·085	99·6
N_2	65·8 37·5 3·9 2·2	10·8 8·3 0·75 0·75	11·0 8·2 1·3 0·75	0·0176	20·5
CH_4	61·6 35·9 4·1 1·3	15·5 10·6 0·7 0·8	15·5 10·6 1·5 0·5	0·009	43·5
CO	64·3 37·1	10·8 7·1	..	0·0069	34·8
A	63·0 36·0	11·8 9·0	..	0·024	19·5
O_2	65·2 36·4	6·1 5·0	..	0·043	8·2

The first conclusion to be drawn from this work is that glass and mica surfaces may be considered, under ordinary conditions, as saturated with gas.

A glass bulb, with internal surface area 180 sq. cm., was evacuated as far as possible at room temperature with a

condensation pump and a liquid air trap. Small quantities
of different gases (nitrogen, hydrogen, oxygen, and carbon

TABLE II

ADSORPTION ON MICA AT 90° ABSOLUTE

Gas.	p microbars.	q obs. mm.^{3}/m.^{2}.	q cal. mm.^{3}/m.^{2}.	$a.$	$b.$
N$_2$	34·0	57·4	57·0	0·156	67·6
	23·8	53·5	53·4		
	17·3	49·0	49·4		
	13·0	44·3	45·1		
	9·5	41·5	40·3		
	7·4	37·6	36·2		
	6·1	33·0	33·0		
	5·0	29·6	29·6		
	4·0	26·3	26·1		
	3·4	23·3	23·5		
	2·8	20·9	20·5		
CH$_4$	122·0	180·9	176·7	0·123	188·0
	83·0	171·5	171·3		
	45·0	157·0	159·1		
	25·8	143·0	143·0		
	17·3	123·9	127·9		
	12·8	105·4	114·7		
	8·0	91·6	93·3		
	5·2	76·0	72·7		
	3·7	63·1	58·9		
	2·7	53·2	47·0		
CO	24·3	93·6	..	0·65	101·3
	16·8	90·9			
A	41·5	37·9	..	0·065	52·1
	28·6	33·9			
O$_2$	42·0	26·1	26·8	0·0805	34·8
	28·4	24·9	24·4		
	4·65	9·1	9·5		
	3·36	7·3	7·4		

dioxide) were then introduced into the bulb at pressure about
10 microbars, and the pressure was continually noted to see
if it diminished. The absorption which took place, if any,

must have been less than 2 per cent. The same result was obtained with mica slips in the bulb.[1]

TABLE III

ADSORPTION ON GLASS AT 90° ABSOLUTE

Gas.	p microbars.	q obs. mm.³/m.².	q cal. mm.³/m.².	a.	b.	a_2.	b_1.	b_2.
N₂ {	73·0 36·5	59·5 } 52·4 }	·· ··	0·088	68·6			
O₂	71·0 35·5 18·5 9·7 5·0 1·3 0·7	36·1 32·0 25·4 17·8 11·3 5·8 3·2	36·4 31·7 25·5 18·6 12·2 4·0 2·2	0·079	43·0			
A	73·0 37·3 19·6 10·6 5·7 2·2 1·0	47·8 38·2 32·0 21·8 13·0 6·1 2·0	47·3 39·4 30·2 21·1 13·6 6·1 2·9	0·0511	60·0			
CO	61·6 31·5 17·3 9·7 5·8 2·7 1·4	101·8 94·1 82·4 71·1 60·0 48·9 42·2	102·8 93·5 82·4 70·6 60·5 48·9 41·7	··	··	0·083	33·6	82·4
CH₄	67·0 34·8 19·3 11·6 7·0 3·4 1·9	103·2 88·0 72·7 57·5 45·8 31·2 22·2	102·8 89·0 73·2 58·5 45·3 30·4 22·5	··	··	0·0638	10·2	114·0

The bulb was then heated and evacuated for one hour at

[1] With mica there was an apparent absorption of oxygen ; but this was found to be due to the little iron distance-pieces between the mica slips.

300° C. (for the cover glasses), and for three hours (with the mica slips). This drove off the amounts of adsorbed gases recorded in a previous paragraph. Then a small amount of gas was introduced as before and the adsorption measured. The temperatures used were room temperature, the temperature of liquid air, and, for the mica only, the temperature of solid ether, 155° Abs.

At room temperature the adsorption was very small at all the pressures used, the range of pressure being between 30 and 110 microbars. With H_2, N_2, A, CH_4, and CO it is less than 0·5 per cent. of the gas introduced. With CO_2 the amount was 1 per cent. (for CO_2 the liquid air must be replaced by solid ether).

At the temperature of solid ether the adsorption of CO_2 is quite appreciable, but it is small for the other gases. The pressures are given in microbars, and are the pressures reached when adsorption suddenly stops (no indication is given of the time this takes). They are thus the equilibrium pressures corresponding to the quantities adsorbed, given in the third column. The quantities are given in cubic mm. at 0° C. and 760 mm. per square metre of surface. The meaning of the numbers in the columns marked a and b is given below.

At the temperature of liquid air (90° Abs.) the adsorption on mica becomes from 3 to 5 times greater, as is shown by the values of b. The adsorption on mica and glass is of the same order, as is shown by the values of b or of $b_1 + b_2$.

The numbers in the fourth column of these tables are the values of q calculated from the following formulæ (the second formula was only used for carbon dioxide and methane, adsorbed at the temperature of liquid air by glass) :

$$q = \frac{abp}{1 + ap} \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

$$q = b_1 + \frac{a_2 b_2 p}{1 + a_2 p} \qquad . \qquad . \qquad . \qquad (17)$$

The first of these can also be written in the form

$$\frac{p}{q} = \frac{1}{ab} + \frac{p}{b},$$

so that $\dfrac{p}{q}$ should be a linear function of p, and the inclination of the graph gives the values of a and b. There is good agreement between the experimental and calculated results, and this confirms to some extent the theory given below.

A Theory of Adsorption founded on the Hypothesis of Condensation and subsequent Evaporation of the Gas Molecules. Langmuir supposes that a gas molecule striking a solid surface does not rebound immediately, but is held at the surface by what may be called chemical forces, or at any rate interatomic forces. This process is identical with that of condensation of vapours on solid surfaces. The reverse process is evaporation. The molecules held at the surface are not absolutely fixed. Both these molecules and the contiguous molecules of the solid vibrate about their mean positions, and the amplitudes of the motions depend on the forces between the gas molecules themselves, and between them and the molecules of the solid. The very rapid energy exchanges which take place due to the action of these forces may endow one of the condensed molecules with a velocity away from the surface sufficiently high to overcome the attractive forces. This particular molecule then becomes an evaporated molecule.[1] The amount of gas adsorbed depends on the state of statistical equilibrium between condensation and evaporation.

Thus only the first layer of gas molecules closest to the surface can be looked upon as definitely adsorbed, since the forces which hold outer layers are the mutual attractions of the gas molecules, with perhaps very small forces exerted by the molecules of the solid at relatively great distances. The molecules in the unimolecular adsorbed layer fill in a kind of chess-board pattern. At a crystal surface they will follow the reticular arrangement of the atoms in the crystal. This

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[1] In another paper (*J. Amer. Chem. Soc.*, 38, 2221, 1916) Langmuir has given a mechanical analogy to this conception. He compares the molecules which are adsorbed to balls attached by springs to a ceiling, and also attached to one another by more springs. If violent agitation is started, some of the balls will get downward impulses which may be large enough to break the springs.

arrangement is as definite as that existing in the interior of the crystal, although slightly different from the latter. The distribution in the interior can in many cases be determined by X-ray analysis.

All the squares of the chess-board pattern may be the same, or there may be a limited number of different kinds (as in crystals), or the properties of the squares may vary continuously (amorphous bodies) : each square may be looked upon as capable of holding a definite number of gas molecules, or, for a diatomic gas, the two atoms in a single molecule may be held in contiguous squares, so that these must be freed together if the molecule is to evaporate (oxygen adsorbed at a metal surface is a case of this) ; lastly, the case of thicker layers may be considered. All these cases can be approached in the same way, and the amount of gas adsorbed can be determined as a function of the pressure. Here we shall only deal with the first case—that is, only one kind of attracting " square," each " square " only holding 1 molecule—and the case of a unimolecular layer.

Let N_0 be the number of " squares " per sq. cm. Thus, in this case, N_0 is the maximum number of molecules which can be adsorbed per sq. cm. Let θN_0 be the number of empty " squares " when statistical equilibrium is reached. Let n be the number of molecules impinging on the surface per sq. cm. per second at a pressure p. If all the molecules striking empty " squares " were held there, the number freshly adsorbed per second would be θn. But only a fraction of these are held, say $a\theta n$. Let n' be the number of molecules which would evaporate per sq. cm. per second if the surface were entirely covered, and let θ' be the fraction actually covered. Then for statistical equilibrium

$$a\theta n = n'\theta'$$

$$\theta + \theta' \doteq 1,$$

and therefore

$$\theta' = \frac{an}{n' + an}.$$

But if n'' is the average number of molecules per sq. cm., then

$$n'' = N_0\theta' = \frac{aN_0 n}{n' + an} = \frac{\dfrac{a}{n'}N_0 \cdot n}{1 + \dfrac{a}{n'}n} \qquad . \qquad . \quad (18)$$

Now n'' is proportional to the amount of gas adsorbed and n is proportional to the pressure. Thus, if q is the volume of gas adsorbed (measured at atmospheric pressure), and p is the pressure of the gas, these must be related by an equation of the form

$$q = \frac{abp}{1 + ap} \cdot \qquad . \qquad . \qquad . \quad (16)$$

From the preceding paragraph it is seen that this equation is verified experimentally, and that a and b can be calculated from the experimental results. From these, by comparison with (18), the values of N_0 and $\dfrac{a}{n'}$ can be calculated. The number of molecules impinging on 1 sq. cm. of surface in 1 second is given by

$$n = \frac{N}{\sqrt{2\pi MRT}}p,$$

where N is Avogadro's number ($6\cdot062 \times 10^{23}$), R the gas constant ($83\cdot15 \times 10^6$), and M is the molecular weight. If V is the volume occupied by a gramme molecule under normal conditions (22,412 c.c.), then

$$n' = N\frac{q}{V},$$

and

$$q = \frac{\dfrac{V}{\sqrt{2\pi MRT}}\dfrac{a}{n'} \cdot N_0 \cdot p}{1 + \dfrac{a}{n'}\dfrac{N}{\sqrt{2\pi MRT}}p},$$

so that

$$a = \frac{N}{\sqrt{2\pi MRT}} \cdot \frac{a}{n'}$$

$$b = \frac{V}{N}N_0$$

$$\qquad \qquad \cdot \qquad \cdot \qquad \cdot \qquad (19)$$

V being expressed in the same units as q, and b relating to 1 sq. cm.

The adsorption of nitrogen on mica at liquid air temperature may be taken as an example (see Table). In this case $b = 67 \cdot 6 \times 10^{-4}$ (the adsorbed volumes in the table being calculated per sq. metre). Substituting

$$N_0 = \frac{67 \cdot 6 \times 10^{-4} \times 6 \cdot 062 \times 10^{23}}{22412 \times 10^3} = 0 \cdot 18 \times 10^{15}.$$

The molecular volume of liquid nitrogen is $35 \cdot 5$ c.c. Dividing this by Avogadro's number and taking the cube root, we get $3 \cdot 88 \times 10^{-8}$ cm. for the side of a cubic molecule. One sq. cm. of surface would contain $0 \cdot 66 \times 10^{15}$ such molecules, that is $3 \cdot 7 N_0$ molecules. Thus the adsorbed layer would only contain $0 \cdot 27$ of the number for a unimolecular layer. The results given in the tables show that in all cases the number of molecules in the adsorbed layer is less than in a unimolecular layer; in most cases it is less than half the number.

The ratio $\frac{a}{n'}$ and a itself have also an interesting physical significance. n' is the number of molecules which would evaporate per sq. cm. per second, if the surface were entirely covered. Thus $\frac{n'}{N_0}$ is the number which would evaporate from one active " square " per second, and $\frac{N_0}{n'}$ gives the average time which a molecule stays on the surface. But only a fraction of the impinging molecules is held, so that, if a is the fraction, only aN_0 " squares " can be looked upon as active. Thus the average number of molecules condensing

per second is $\dfrac{n'}{aN_0}$, and the mean life of the molecules on the surface is given by

$$\tau = \frac{aN_0}{n'} = \frac{N_0}{N}\sqrt{2\pi MRT} \cdot a.$$

Thus the values of τ can be calculated from those of a and b. The times are of the order of 10^{-4} second.

Instead of considering the values of τ we may consider the time which 1 gramme molecule of gas would take to evaporate from 1 sq. cm. of surface. Let this time be σ. During a time τ the number of molecules evaporating per sq. cm. is N_0, since there are N_0 " squares." Thus the time for the evaporation of a gramme molecule of gas is given by

$$\sigma = \tau \frac{N}{N_0}.$$

Langmuir calls this the " relative life " of a gramme molecule on the surface. From his experimental results he finds values of σ of the order of 100,000 seconds. This time is much longer than that taken for the evaporation of 1 gramme molecule from the surface of the liquefied gas at the same temperature. This shows that the forces which hold adsorbed gas molecules at solid surfaces are far greater than those experienced by the molecules in a liquid surface in contact with the vapour from the liquid.

We see also that, since n' is proportional to the rate of evaporation of the adsorbed gas, it should increase rapidly with temperature ; and that the mean life τ and the relative life σ should decrease very rapidly with rising temperature, as also should q, the amount of gas adsorbed. This explains the effect of heating in the elimination of surface gases *in vacuo*.

Equation (17), which contains three coefficients, a_2, b_1, and b_2, and is used for the adsorption of carbon dioxide and methane, may be obtained in a similar way to equation (16), by supposing that there are two different kinds of " squares " on the surface.

Adsorption on Silicates other than Glass and Mica. Very few results are available relating to the above. Briggs [1] has studied the adsorption of various gases and water vapour by pulverised quartz. Katz [2] has studied the adsorption of quartz and anorthite. The adsorbed layers, like those on glass, are from 10 to 200 molecules thick.

Adsorption by Metals and Occlusion. It is well known that when metals are heated *in vacuo* they give off quite appreciable amounts of gas. In order to measure the gas driven off, care must be taken in order to avoid heating the containing vessel. Thus the best way is to use a filament heated by an electric current, inside a large bulb.

The phenomenon is very complex, and changes a good deal with different conditions. There may be the driving off of a surface layer, as with glass, or the liberation of gas dissolved in the metal, or the expulsion of gas which was chemically combined with the metal, etc. Simple adsorption seems to be less important with metals than with glass and silicates, or, at any rate, the mechanism seems different.

In his paper on the adsorption of gases at solid surfaces at low temperature, Langmuir [3] describes a large number of experiments, similar to those on glass and mica, on adsorption of gases by pure platinum. The platinum used was a piece of pure platinum foil of thickness 0·01 mm. and surface area 312 sq. cm. The foil was cleaned by heating to a bright red heat for several minutes in a bunsen flame, boiling in hydrochloric acid, and finally washing thoroughly in distilled water. The sheet was crumpled and placed inside a tube, which was joined on to the same apparatus as that used for the experiments with glass. After exhausting and drying (using a liquid air trap) for twenty-four hours the platinum was baked for one hour at 350°, with the condensation pump operating continuously. This heating caused the evolution of 18·3 cu. mm. of hydrogen, 5·8 of carbon monoxide, 17·7 of carbon dioxide, 92 of water vapour, and 1·2 of some non-condensable gas, probably nitrogen. A similar heating of the

[1] Briggs, *J. Phys. Chem.*, 9, 617, 1905.

[2] Katz, *Proc. Acad. Amsterdam*, 15, 445, 1912.

[3] I. Langmuir, *J. Amer. Chem. Soc.*, 40, 1361, 1918.

empty bulb gave only 55 cu. mm. of water vapour, 4·6 of carbon dioxide, and 0·5 of nitrogen. Thus the amounts from the platinum itself may be taken approximately as 37 cu. mm. of water vapour, 13·1 cu. mm. of carbon dioxide, 5·8 cu. mm. of carbon monoxide, 18·3 cu. mm. of hydrogen, and 0·7 cu. mm. of nitrogen.

Do these gases come from adsorbed layers ? This seems doubtful, because after this purging the foil showed no signs of adsorption, even at the temperature of liquid air, for hydrogen, oxygen, and carbon monoxide. Water vapour was not tried.

But when the platinum was heated to about 130° C. in a previously introduced mixture of hydrogen and oxygen at low pressure, not only do the gases begin to combine, but the platinum itself assumes new properties. It is said to be activated. That is, it would now cause combination of these gases at room temperature, and also of carbon monoxide and oxygen. The quantities of oxygen and carbon monoxide which disappeared when the gases were brought into contact with the platinum were not in the stoichiometric ratio, but depended on the previous history of the platinum. Thus, if the platinum had previously been in contact with the oxygen, an abnormally large amount of carbon monoxide disappeared when a mixture was introduced into the bulb. Similarly, after an excess of carbon monoxide had been used, there was an abnormal disappearance of oxygen.

The quantities of oxygen and carbon monoxide which were adsorbed by activated platinum corresponded to monomolecular layers. These quantities seem to be strongly held, and cannot be driven off altogether, even *in vacuo* at 300° C. A layer of adsorbed oxygen is transformed immediately to carbon dioxide if carbon monoxide is let in. The same thing happens to a carbon monoxide layer when oxygen is let in.

Since these phenomena are more important in the study of catalysis and chemical combination than in vacuum work, the description of them has been cut down to the few extracts given above. They show how complex these phenomena are.

Although a great deal of work has been done on the absorption and solution of certain gases (in particular hydrogen) by metals, there is no way of calculating the amounts of gas which will be given off when a metal is heated. The cases of platinum black and palladium black are not treated here, but in Chapter IV, since they are used for improving vacua, by absorption at low temperatures. The cases dealt with below are those in which, in practice, it is important to drive off as much of the surface gases as possible, as in lamp filaments, and in the metal parts of Coolidge bulbs and thermionic valves.

If a tungsten filament lamp is taken and the filament raised to incandescence before the walls of the bulb have been cleared of water vapour by heating *in vacuo*, it is found [1] that an amount of hydrogen is produced which is many times the volume of the filament. The hydrogen is formed by the decomposition of the water vapour which evaporates from the walls, which oxidises the tungsten. If the bulb is first heated at low pressure for an hour at 360° C., the gases liberated when the filament is raised to 1500° C. will only occupy a volume from three to ten times that of the filament. They also come off almost instantaneously, and the bulk of the gas in this case is carbon monoxide (70 to 80 per cent.); the rest is mainly carbon dioxide and hydrogen.

With a platinum filament under the same conditions the volume of gas driven off is not more than one-tenth of the volume of the filament.

Sweetser [2] has measured and analysed the gases driven off in this way by filaments of different metals raised to incandescence *in vacuo* until no more gas is given off. Wires of nickel, copper, " monel " metal, and platinor, used as current leads in incandescent lamps, give off between 3 and 20 cu. mm. of gas: that is less than the volume of the filament. The composition of the gases driven off is: carbon monoxide, 75 to 90 per cent.; carbon dioxide, 10 to 20 per cent.; and small quantities of hydrogen.

Similarly, the copper anodes used in Coolidge bulbs gave

[1] I. Langmuir, *J. Amer. Chem. Soc.*, 35, 105, 1913.
[2] See Dushman, *Gen. Elect. Rev.*, 24, 252, 1921.

off gases in the following proportions : carbon monoxide, 92 per cent.; carbon dioxide, 7 per cent.; nitrogen and hydrogen together, 1 per cent.

But, according to Ryder,[1] commercial copper heated *in vacuo* gives off carbon dioxide, carbon monoxide, water vapour, and nitrogen in order of quantities, the total volume being about one-sixth of that of the metal. Moreover, at 750° C. copper gives off large quantities of oxygen, no doubt due to the decomposition of cuprous oxide, present in the metal.

Therefore all surface gases must be driven off as completely as possible from all metal parts of a vacuum apparatus before it is sealed off, particularly if the metal is heated when the apparatus is used. This is easy with lamp filaments, but the current leads cause some difficulty, because they are not heated to a high temperature during the making of the lamps, and so they give off slowly small quantities of gas when the lamp is in use. These small quantities can be got rid of by putting suitable absorbers inside the bulb (Chapter IV). In the case of thermionic valves and X-ray bulbs the heating is done by electron bombardment, which enables high temperatures to be reached. Unfortunately, this method of heating is not always convenient. No doubt, heating by eddy currents would be the best solution and the most generally applicable, but it involves the use of costly and complicated apparatus. In short, the construction of each type of apparatus should be arranged so that, as far as possible, all metal parts may be heated *in vacuo* before sealing off.

Since the bulk of the gas occluded by metals is carbon monoxide, it would probably be advantageous to heat the metal parts *in vacuo* before they were fixed to the apparatus. I do not know of any data relating to the quantities and nature of gases which metals would give off on heating *in vacuo* after being first treated in this way. It seems probable that the carbon compounds are driven off once for all.

8. **The Microanalysis of Gases.** In a great number of researches on vacuum work it is important to know the

[1] Ryder, *J. Amer. Chem. Soc.*, 40, 1656, 1918.

composition of the gases which are present at very low pressures. The microanalysis of gases is continually employed in American industrial laboratories in research work on incandescent lamps, on the emission of occluded gases by heated metals, on the adsorption of gases, and on chemical reactions at very low pressures. The gases measured by the methods in use are hydrogen, oxygen, carbon dioxide, carbon monoxide, and water vapour ; it is possible also to determine the amount of hydrocarbons present, this being usually taken to be methane ; the residue after analysis, which is gas which is not condensed by liquid air, is usually taken to be nitrogen.

Langmuir and Ryder's Method. Langmuir makes many references to his method of microanalysis, but he gives very few details. The apparatus in which the gas is evolved is joined, through a U tube dipping into liquid air, to a Toepler pump and a McLeod gauge. " The apparatus [1] was so designed that the gases delivered by the pump could be collected over mercury and mixed with either oxygen or hydrogen, and brought into contact with a glowing platinum wire, and returned into the vacuum system without coming into contact with any stopcocks or any substance other than glass, mercury, or platinum. With this apparatus we are able to make quantitative analysis of amounts of gas as small as 1 cu. mm., determining the following constituents : H_2O, CO_2, CO, H_2, O_2, and N_2 (the latter by difference). The errors of the analysis are less than 5 per cent. with 1 cu. mm. of gas, and much less when larger quantities are used." A little later on the author gives the following rather scanty details :—" The usual method of analysis of gases was as follows : The gas was pumped over into a small bulb of about 1 c.c. capacity, which contained a short piece (2 mm.) of very fine platinum wire. This wire was brought to a dull red heat for a couple of minutes, and the gas was then allowed to return to the system, and readings were taken on the McLeod gauge to see if there had been any contraction. Such contraction would denote the presence of oxygen, together with carbon monoxide or hydrogen. The carbon dioxide or water vapour produced by such a combination would be

[1] I. Langmuir, *J. Amer. Chem. Soc.*, 34, 1310, 1912.

condensed by the liquid air. Then a measured excess of pure oxygen was admitted and the reading again taken on the gauge. In any ordinary analysis the amount of gas calculated from the increase in pressure indicated by the gauge would agree closely with the measurement of the volume of oxygen made before admitting it to the system. The mixture of oxygen with the sample of gas was now again pumped over to the small ignition bulb and the wire brought to a red heat. After allowing the gas to again return to the system, and permitting the liquid air to condense the carbon dioxide or water vapour formed, the gauge was again read. Two-thirds of the contraction gave the amount of hydrogen plus carbon monoxide. By replacing the liquid air by solid carbon dioxide in acetone, the carbon dioxide in the system was liberated, while the water vapour was held back. From the increase in pressure the amount of carbon dioxide could be calculated, and from this was found the amount of carbon monoxide originally present. As the sum of the hydrogen and carbon monoxide was known, the amount of hydrogen could now be calculated.

" This method of analysis proved extremely reliable and satisfactory for all gases liberated within the bulbs of lamps, except after the filament had been heated in the bulb for a long time in the presence of a gas containing hydrogen." This exception relates to the " activity " assumed by hydrogen under these conditions. According to Langmuir, who has done a good deal of work on this point, the " activity " is due to atomic hydrogen.

Although Langmuir does not expressly say so, it appears that the amount of water vapour was determined from the difference between the pressure in the system when liquid air surrounded the U tube and the pressure arrived at when the U-tube bath was changed to solid carbon dioxide in acetone ; and these pressures were measured by a McLeod gauge. But even small traces of water vapour entirely vitiate the readings of a McLeod gauge, so that this seems to be a rather serious defect in the method, unless the water vapour is determined in some other way not mentioned in Langmuir's paper.

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Ryder [1] has given fuller details of the same method.   The difficulty about measuring water vapour is got rid of by using an optical lever gauge.   Fig. 68 shows the part of Ryder's apparatus used for gas analysis.

The oxygen introduced was produced by electrolysis, and the carbon monoxide from sulphuric acid and formic acid. The following is the order of manipulation : The mercury
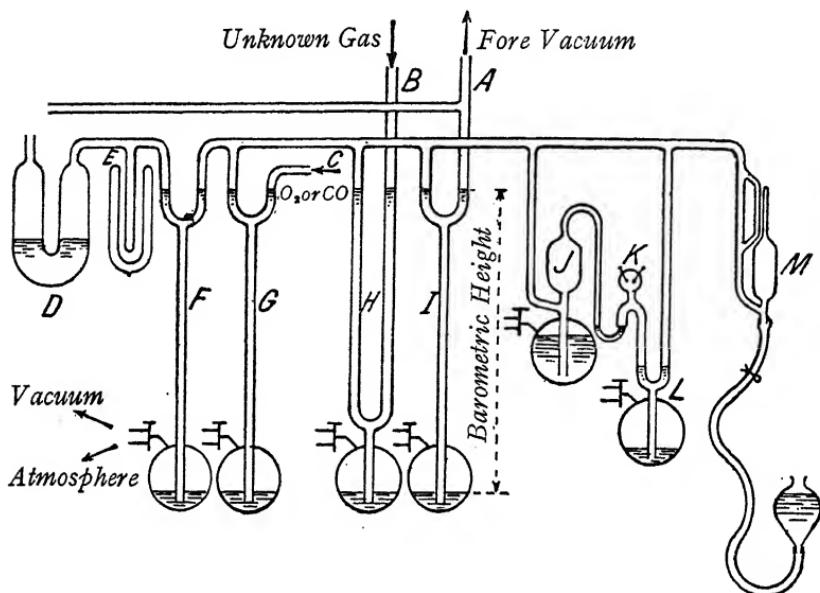

FIG. 68.

cut-offs, F, G, H, I, L, are lowered, that is opened, and the whole apparatus is evacuated as far as possible, as are also the bulb where the gases are going to be driven off and the connecting tubes to the apparatus producing the known gases. Then I and G are closed, so that the analysing apparatus and the apparatus for O_2 and CO are cut off from the pump. The gases for measurement are then driven off and can be sent in at B ; they may be, for example, the gases given off by an incandescent filament.   These gases expand through the apparatus, and the carbon dioxide and water vapour in them

[1] H. M. Ryder, *J. Amer. Chem. Soc.*, 40, 1656, 1918.

condense in the trap E, which is surrounded by liquid air. The pressure of the non-condensable gases is measured by the gauge M. If the volume of the tube system is known, the volume they would occupy under N.T.P. conditions can be calculated. Then the Toepler pump J is worked (the lower reservoir of J can be put into communication with the atmosphere, and also with the fore vacuum), and the gases are drawn into the little bulb K, which contains a little platinum filament. During this operation L is of course closed. Then the carbon dioxide condensed in E is allowed to evaporate by changing the bath round E to carbon dioxide snow in acetone. The pressure of the carbon dioxide is measured by M, and then it is driven out at A by means of the high vacuum pump, after lowering I, which is closed when this operation is completed. F is then closed and the bath is taken from the trap E, which then rises to room temperature. The optical lever manometer D will now measure the pressure exerted by the water vapour, and its volume under N.T.P. conditions can be calculated if the volume of the right-hand limb of the manometer, together with that of E and the left limb of F, is known. Thus the quantities of CO_2 and H_2O are determined. The liquid air bath is replaced round E, and the cut-off F is again opened.

The gases in K, which are not condensed by liquid air, remain to be analysed. Suppose that oxygen and a hydrocarbon do not both occur in the gases. By opening the cut-off G a measured quantity of oxygen is let in at C. As a check its pressure in the tube system is measured. It is then drawn into K by means of the Toepler pump. The platinum filament is heated so that combustion will take place in K, and then the cut-off L is opened to allow the carbon dioxide and water vapour produced by combustion to flow back into the tube system, together with the excess of oxygen and any incombustible gas which may be present. The water vapour and carbon dioxide are condensed in E, and the pressure of the residual oxygen and the non-combustible gas is measured, and then these are again drawn into K. The quantities of carbon dioxide and water vapour are measured as before (the amount of H_2O by the difference between the last and

first amounts condensed). These give the amounts of carbon monoxide and hydrogen in the given mixture. If the mixture is known to contain a definite hydrocarbon, say CH_4, the amounts of carbon dioxide and water formed will give the amounts of CO, CH_4, and H_2, if the total volume of these is known, *i.e.* the volume of non-condensable gases at liquid air temperature. Thus the procedure in both cases is the same, but the method of calculation is different. In all case the amounts of carbon dioxide and water vapour found give the amount of oxygen used in combustion. This is subtracted from the quantity let in to the tube system. If the origin mixture contained neither oxygen nor nitrogen nor any c the monatomic gases, this difference should represent the amount of gas in K, and the last measure with the gaug gives the volume of this. It is thus ascertained whether the mixture contained one at least of the following gases : oxygen nitrogen, or gases of the zero group.

If the original mixture contained neither oxygen nor nitrogen, the analysis is finished. If not, the difference between the oxygen let in and the oxygen used up is less than the volume of gas in K. When this happens a measured excess of carbon monoxide is introduced into K and com- bustion is assured as before, and then the bulb is put into communication with the rest of the system. The CO formed is measured as before, and the corresponding quantit of oxygen is calculated. If the mixture contained no oxyge this should be equal to the difference between the oxyge introduced and the oxygen used. If the amount got by calculation is greater than this difference, the excess gives the amount of oxygen in the mixture. In all cases the dif- ference between the total quantity of the mixture introduced and the sum of the quantities of CO_2, H_2O, etc., found by the analysis is taken as the amount of nitrogen present.

If a hydrocarbon is present as well as oxygen, the method has to be modified.

The following is an example of the analysis : The gases were given off by a filament of silicon steel heated to be- tween 750° C. and 800° C. The pressures are in tenths of microns.

H_2O condensed and separated	.	.	o		(1)
CO_2 ,, ,, ,,	.	.	33·5—that is 3·86 cu. mm.		(2)
" Dry gases "	.	.	. $\{$ 898		(3)
O_2 added	.	.	. $\{$ 535		(4)

Total   1433   (5)

Amount remaining after combustion
   and condensation of H_2O and CO_2
   produced   605   (6)

Contraction resulting from formation
   of H_2O and CO_2 .   .   .   828   (7)
$\frac{1}{3}$ of this is oxygen used up   .   .   276   (8)
$\{$ $\frac{2}{3}$ represent $CO+H_2$.   .   .   . $\{$ 552   (9)
$\{$ The CO_2 formed is then evaporated, the $\{$
   equivalent amount of CO   .   . $\{$ 437   50·3 cu. mm.   (10)

H_2 by difference   115   13·22 cu mm.   (11)
$\{$ Total " dry gases " (3)   .   .   . $\{$· 898
$\{$ $CO+H_2$ (9)   .   .   .   ., . $\{$ 552

Difference N_2+O_2   346   39·8 cu. mm.   (12)
   O_2 added (4)   535
   O_2 used (8)   276

Difference   259   259   (13)
259 < 346 ∴. add CO.
$\{$ " Dry gases " according to (6) (N_2+O_2) $\{$ 605
$\{$ CO added   .   .   .   .   . $\{$ 1583   (14)

Total   .   .   .   2188   (15)

Quantity remaining after combustion
   and condensation of CO_2 formed   .   1415   (16)

Quantity disappearing due to formation
   · of CO_2   773   (17)
$\frac{1}{3}$ of this is O_2   258   (18)

Thus the mixture contained no free oxygen, and its
composition was

H_2O	o		o per cent.	
CO_2	3·86 cu. mm.		3·6	,,
CO	50·30	,,	46·85	,,
H_2	13·22	,,	12·35	,,
N_2	39·80	,,	37·20	,,

In order to test the accuracy of the method the author
applied it to analyse mixtures of H_2, CO, and O_2 in known
proportions. With 5 cu. mm. as total volume the error in

the determination of the predominant gas in the mixture may be as much as 6 per cent.   This is less than the accuracy claimed by Langmuir (see above).

Guye's Apparatus.   Guye and Germann's [1] apparatus has a kind of Toepler pump M (fig. 69), combined with a McLeod
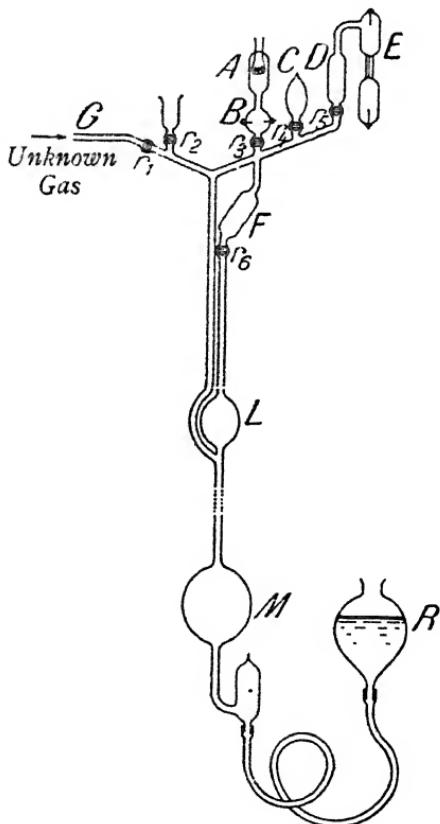
FIG. 69.

gauge L, which has its compression chamber closed by a tap instead of being sealed off.

This tap is marked r_6 in the figure.   The unknown gas is let in at G through the tap r. A is a bulb containing a spiral of iron wire for taking up oxygen; B is a combustion vessel, with platinum electrodes, for the combination of oxygen and

[1] Ph. A. Guye and Germann, *J. de Chim. Phys.*, 14, 194, 1916.

combustible gases; C is a small bulb containing very tiny fragments of caustic potash for absorbing carbon dioxide; and E is a discharge tube for examining the spectrum of the gases. Between E and the rest of the apparatus is a tube D, containing gold leaf which absorbs mercury vapour. The bulb in which the gases are produced is joined on at G, and the apparatus is evacuated by using the pump RML. This is done by opening all the taps and lifting R until the mercury level in the system is at r_2. The air is forced out at this tap. r_2 is then closed, and R is lowered. Now r_1, r_3, r_4, and r_5 are closed, and R is again raised, the air being driven out at r_2 as before. Then r_2 is closed, and r_1, r_3, r_4, and r_5 are opened and R lowered. After a number of such operations the pressure reached can be measured in L. Quite low pressures can be reached.[1] The tap r_6 is closed when the gauge is in use.

The gas for analysis is produced in the bulb to the left of G, whilst r_2, r_3, r_4, and r_5 are closed. The gases must now be transferred to the tubes to the right of r_1. This is done by closing r_1, and raising R after opening r_3. The gas in the connecting tubes to the right of r_1 will be driven into B. By closing r_3 again and opening r_1, and lowering R and then repeating the flushing into B, more of the gas from G will be collected in A and B. After several strokes of the pump the amount of gas to the left of r_1 will be negligible. After the last stroke R is lowered and r_6 is closed, and the pressure of the gas is measured. The volume of the system is known (it is got by joining a bulb of known volume on at G, and applying Boyle's Law after expansion and pressure measurements), and so the volume of the mixed gases under atmospheric pressure can be calculated. All the gas is then driven into B by raising R until the mercury level inside rises to r_3, and the iron spiral is raised to incandescence. The pressure is then measured again, and thus the amount of oxygen in the mixture may be calculated. The same set

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[1] The limiting pressure reached is obviously not comparable with the pressures reached in the experiments described in the preceding pages. This apparatus was designed to analyse at least 20 or 30 cu. mm. of gas, and the gauge was only made to read down to 0·01 mm.

of operations repeated for the bulb C enables the amount of carbon dioxide to be calculated. If other gases are present, either oxygen or hydrogen is introduced, and the measurements of pressure obtained after combustion. However, the apparatus has not been very much used. The authors have published only analysis of dry air as a trial of the apparatus. The measurement and elimination of water vapour seem to need some improvement. The authors state that the errors were about 1 in 200 when analysing 120 cu. mm. of dry air. This apparatus would appear to be worth further development, although its apparent simplicity is partly due to the use of taps, which should be abolished in accurate work.

N. R. Campbell's Method. The methods given above use a McLeod gauge for measuring the total or partial pressures of the gases, and this means eliminating water vapour, because it falsifies the readings of the gauge. The method used in the laboratory of the English General Electric Co. [1] employs a single manometer for measuring both the vapour tensions and the pressures of the permanent gases. The method depends on the determination of the dew-points of the different gases, condensable at the temperature of liquid air, which are of practical importance in vacuum work. The manometer used is the Pirani gauge (see Chapter II).

A small size tube is attached to the gauge, the volume of this tube being small compared with that of the gauge. The small tube is cooled to a very low temperature and then allowed to warm up slowly. If the pressure temperature curve were drawn, it would be like that in fig. 70. The temperatures at which the sudden rises in the curve occur serve to identify the vapours present, since they correspond to the dew-points of the different condensed vapours. For example, when the side tube rises above $(T_0)_2$, vapour (2) comes off, and its pressure will then vary only slowly with the temperature. From the temperatures $(T_0)_1$, $(T_0)_2$, etc., the different constituents may be identified, and the difference between the pressures p_1, p_2, p_3, etc., corresponding to the heights of the different steps, will give the partial pressures of the constituents. The graph will not be strictly like that of

[1] Research Staff of Gen. Elect. Co., London, *Proc. Phys. Soc.*, 33, 287, 1921.

fig. 70, which is drawn to illustrate the principle of the method.   There will be no sharp discontinuities at the points A_1, A_2, A_3, etc., and the lines, such as A'_1, A_2, A'_2, A_3, will not be strictly horizontal.   Suppose the gas is not a mixture, but a single gas.   The pressure curve below the dew-point will be the " steam-line " of the substance : that is, the graph of saturation pressure against temperature.   Above the dew-point the curve will be the expansion curve of the
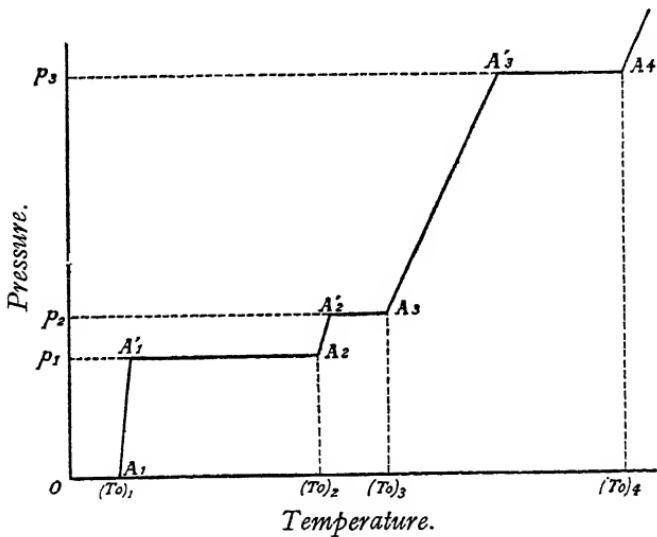
FIG. 70.

vapour, which will then be unsaturated.   Thus, A'_1, A'_2, etc., would be sharp discontinuities theoretically.   The steps, such as A'_1, A_2, will correspond to the expansion of unsaturated vapour, together with the variation of saturation pressure with temperature of the condensed vapours.   The interval will, however, correspond to a temperature range for which the saturation pressure is small and varies only slowly with the temperature.   The rapid rises, such as A_1, A'_1, will correspond to the same two variations, but in this case to a range during which the saturation pressure of one constituent varies rapidly with the temperature, since the vapour is approaching the dew-point.   Thus, if the procedure is to allow the condensed mass to warm up, the beginnings of the steps, A'_1,

A'_2, A'_3 will correspond to the dew-points and not the other points, A_1, A_2, A_3, where there will be no sharp discontinuities, although Campbell takes the last set. According to Campbell the variations in saturation pressures of the liquefied gases met with in vacuum work are such that A_1, A_2, A_3 are sharp discontinuities, and A'_1, A_2, etc., are practically horizontal, so long as the pressure of any one constituent does not exceed 0·1 mm. at room temperature. The method is recommended for total pressures between 0·1 mm. and 0·001 mm.

If the assumption is true that " the pressure of each vapour present rises from zero to the maximum, fixed by the total amount of the substance present, in the interval between T_0 for that substance and T_0 for the substance of next higher condensation temperature," the differences between the heights of the steps—that is, between the pressures p_1, p_2, p_3, etc.—will, as stated above, be the partial pressures of the different vapours. If the method is to work it is obvious that all the gases in the mixture, except one at most, must be easily condensable by liquid air. Thus the hydrogen must be changed into water vapour and the carbon monoxide into carbon dioxide. In order to do this the bulb contains a copper wire, coated with cuprous oxide, which is heated to redness. This filament takes up the oxygen in the mixture, if any, at the same time. The method is quite satisfactory for H_2 and O_2, but the CO does not seem always to be converted wholly into CO_2.

The Pirani gauge has already been described in Chapter II together with the method of using it and of calculating the values of the quotient $\dfrac{(V^2 - V_0^2)}{V_0^2}$, in which V_0 is the difference of potential between the ends of the filament when the pressure in the bulb is as low as possible, and V is the potential difference when the gas is in the bulb. The method of drawing calibration curves for different gases, by plotting $\dfrac{(V^2 - V_0^2)}{V_0^2}$ against the pressure, has also been described. These curves are sensibly straight lines (fig. 48), and the curve for CO practically coincides with that for CO_2.

The following details of procedure are given in Campbell's paper (*loc. cit.*).

Instead of measuring the dew-points on a fixed temperature scale, it is much easier to compare the indications of the gauge containing the unknown mixture with those of similar gauges each containing a known gas, or even a mixture of gases which do not react chemically. " The side tubes from the series of known vapours and the side tube from the gauge under analysis are then immersed in a little mercury in a small Dewar flask, and liquid air poured in until the whole is cooled to the temperature of that liquid. The conductivity of the mercury is sufficient to maintain all the side tubes at the same temperature. The mercury is then warmed by blowing air at a suitable rate on its surface, and the unknown gauge is watched until a sudden change in (V^2) occurs. The air stream is stopped temporarily and the known gauges examined to discover in which of them (V^2) has changed. If several have changed from their liquid air values, the constituent in the unknown gauge is, of course, that one in these known gauges which has the highest T_0.

" This method is extraordinarily sensitive and certain. One per cent. of water in CO_2 may be detected—an unfavourable case, because the main constituent evaporates before the impurity ; 0.0005 mm. of CO_2 may be detected in an unlimited quantity of vapours with higher T_0, or in 0.05 mm. of permanent gases. On the other hand, mercury vapour is not easy to detect. Apparently its cooling effect is very small. But it is usually known without analysis whether mercury is present, and, if so, how much.

" If the constituents are known, the estimate of their amounts can be made very rapidly. A series of baths are prepared at temperatures which lie between the T_0's for the constituents ; the side tube is then placed in the baths in succession, and the change in (V^2) in passing from one bath to another gives the amount of vapour with a T_0 between the temperatures of the two baths.

" Thus, in order to analyse a mixture containing (1) phosphorus vapour, (2) water, (3) a vapour not chemically identified from vacuum oil, (4) CO_2, (5) H_2, (6) CO, the following

baths will serve, in conjunction with the oxidised copper wire :—

"Freezing mercury ($-39°$) condenses phosphorus, but not water.

"Freezing acetone ($-95°$) condenses water, but not oil vapour.

"Freezing ethyl alcohol ($-117°$) condenses oil vapour, but not CO_2.

"Liquid air ($-183°$) condenses CO_2, but not permanent gases.

"For some purposes an interpolation between the first two baths might be necessary. Then it is convenient to know that freezing chloroform ($-65°$) is just above, and solid CO_2 ($-78°$) just below, T_0 for water. Greater difficulty arises in interpolating between the last two baths in the table, but, so far, we have not found need for such interpolation. In order to prepare the baths, a few drops of the liquid are placed in a Dewar flask, and liquid air poured in (very gently with the lighter liquids) until the solid separates."

After the different values of V have been measured the side tube is sealed and taken off (cooled in liquid air). The measurement of the pressure in it would give the partial pressure of nitrogen. Campbell does not seem to have taken any measurements for nitrogen, and gives no calibration curve for it. The bulb is then evacuated to find V_0.

"Finally, we may give details of the analysis of a mixture containing H_2, CO, H_2O, CO_2.

	V.	V^2.	(V^2).	Diff.
Side tube at temp. of room .	5·09	25·91	6·87	
				3·75
Freezing acetone . . .	3·68	13·54	3·12	
				0·92
Liquid air	3·24	10·54	2·20	
After heating Copper Oxide.				
Room	5·00	25·00	6·60	
				4·83
Freezing acetone . . .	3·02	9·12	1·77	
				1·76
Liquid air	1·82$_2$	3·31$_9$	0·00$_8$	

Gauge exhausted on to pump < 0.00001 mm.

$$1.81_5 = V_0.$$

From the calibration curves $p = a\dfrac{V^2 - V_0{}^2}{V_0{}^2}$ (per mm. Hg.)

with $a = 0.0121$ for H_2

,, $a = 0.0174$,, H_2O

,, $a = 0.0211$,, CO and CO_2

$\therefore$ H_2O present originally $= 3.75 \times 0.0174 = 0.065_2$ (0.061).

CO_2 ,, ,, $= 0.92 \times 0.0211 = 0.019_5$ (0.018).

H_2O produced by burning—

H_2 present originally $= (4.83 - 3.75) \times 0.0174 = 0.018_8$ (0.020).

CO_2 produced by burning—

CO present originally $= (1.76 - 0.92) \times 0.0211 = 0.017_6$ (0.020).

Total   .   . $= 0.121_1.$

The figures in brackets are the pressures of the gas estimated when the gauge was filled for this test.

Observe that the value of (V^2) for the permanent gases originally present should be

$$\frac{0.0188}{0.0121} + \frac{0.0176}{0.0211} = 1.55 + 0.84 = 2.39.$$

The value found was 2.20."

This method is obviously attractive. An analysis like that given above only takes half an hour.

In conclusion, it may be stated that the published figures, relating to the methods of analysis given above, give no definite idea of the accuracy of the methods. It should be between 5 and 10 per cent. on the average.

CHAPTER IV

THE PRODUCTION AND IMPROVEMENT OF VACUA BY ABSORBERS AND BY ELECTRIC DISCHARGE

1. **The Use of Charcoal at Low Temperature.** The absorption of gases by charcoal which has previously been cleared of gas is well known. Sir James Dewar,[1] in 1875, showed that this property of charcoal could be used to reach low pressures, but the method was not used in laboratory practice until the use of liquid air became common. Dewar [2] gave the method of preparing the charcoal, and recommended the use of cocoanut charcoal. Before the invention of Gaede's molecular pump, Dewar's method was the usual way of reaching very low pressures. It is much less common nowadays, because the limiting pressure reached is not appreciably lower than that with molecular pumps and condensation pumps in conjunction with liquid air traps, and because it is less convenient and much slower. Thus, only the results obtained with different gases and the preparation of the charcoal are dealt with below. A good deal of work on this process was done during the war in order to obtain the best possible gas masks.

Preparation of Charcoal. "*Activated*" *Charcoal.* The method of preparation given by Travers [3] is as follows :—

The soft part of the cocoanut is heated in a muffle furnace for several hours at just below a red heat until no more vapour is given off ; then the temperature is raised to a dull red heat for about half a minute. The charcoal is then introduced

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[1] Sir J. Dewar, *Nature*, 15th July 1875.

[2] Sir J. Dewar, *Proc. Roy. Soc.*, 74, 122, 1904.

[3] W. Travers, *Proc. Roy. Soc.*, 78, 9, 1907.

in the absorbing tube, which should be furnished with a good tap. It is then heated to 440° C. (bath of boiling sulphur) for several hours *in vacuo*, and the tap is then closed so that no air reaches the carbon before it is used.

The only improvement arrived at by the chemical branches of the War Services was the substitution of the cocoanut shell for the soft part of the nut. The charcoal from the shell is much denser and absorbs much more gas than that from the soft part. The absorbing power of a given sample is not constant during its use. Lemon [1] observed the following phenomena :—

1. The absorbing power grows up to a certain limit if the charcoal is allowed to absorb air several times at the temperature of liquid air, each absorption being followed by a purging of the sample by heating *in vacuo*.

2. The temperature of purging must not be too high, or the absorbing power may decrease. If the charcoal is heated above 900° C. *in vacuo* it loses all its absorbing properties.

3. This loss of absorbing properties does not correspond to a permanent change. The charcoal can be " activated " again to a large extent by beginning over again the cycles of absorptions and lower temperature " purgings " (650°).

These phenomena are shown graphically in figs. 71, 72, 73, and 74. The curves in figs. 71 and 72 relate to the absorption of atmospheric air by 26 grammes of cocoanut charcoal, carbonised at 850° for one hour, and then placed in a silica tube which is sealed on to the tube system. The air was introduced at approximately atmospheric pressure, after the silica tube had been immersed for thirty minutes in liquid air, so that the granules of charcoal would read liquid air temperature. The abscissæ are the logarithms of times, starting from the moment of letting in the air, and the ordinates are the logarithms of pressure in centimetres of mercury.

The relative amount of gas was not sufficient in any case to produce saturation of the charcoal.

Figs. 71 and 72 show very well the improvement produced by a series of absorptions, and then purgings at 600° C. for

[1] Lemon, *Phys. Rev.*, 14, 281, 1919 ; and Lemon and Blodgett, *Phys. Rev.*, 14, 394, 1919.

four and a half hours. This duration of purging resulted in a pressure of 80μ being reached at $600°$, $0·08\mu$ at $400°$, and a pressure too small to be measured at room temperature. Fig. 72 shows that the improvement of the vacuum is slight
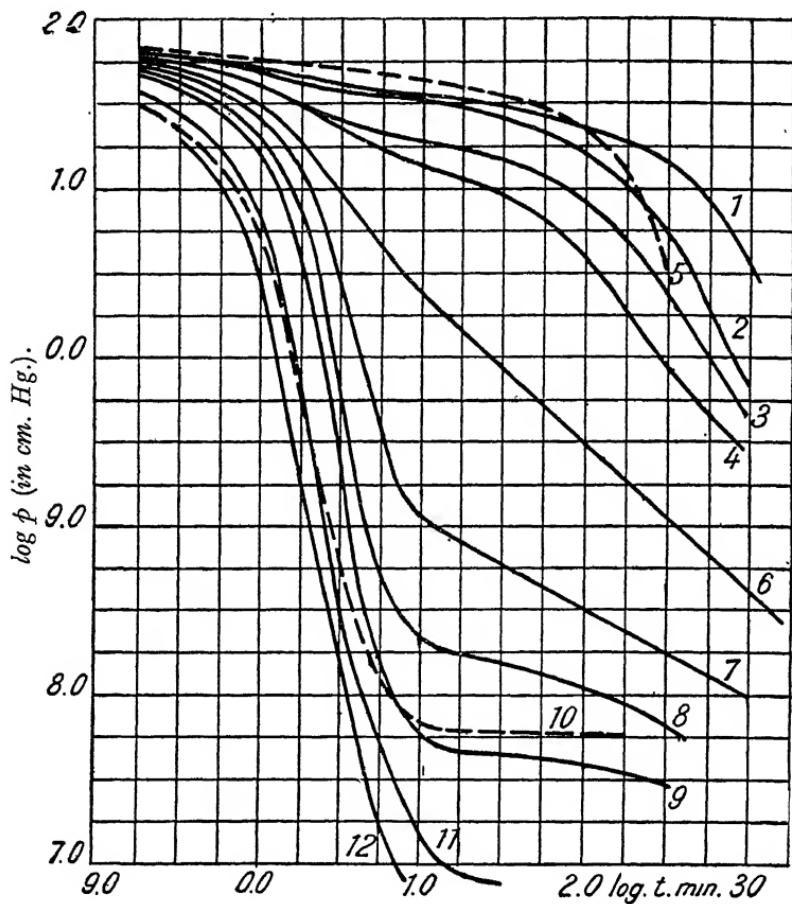
FIG. 71.

between the 14th and 17th purgings. The pressure reached is between $0·01\mu$ and $0·001\mu$, and this takes a little over thirty minutes. The 18th and 19th purgings give similar results. The 20th purging was performed at $1200°$, and the absorption was then measured as before. The curve marked 20 shows that the absorption was then practically nothing.

At temperatures not quite so high as 1200° the loss of absorbing power is more gradual. This is shown in fig. 73, which gives the data obtained with a sample carbonised for three hours at 670°. The first curve shows great absorption,
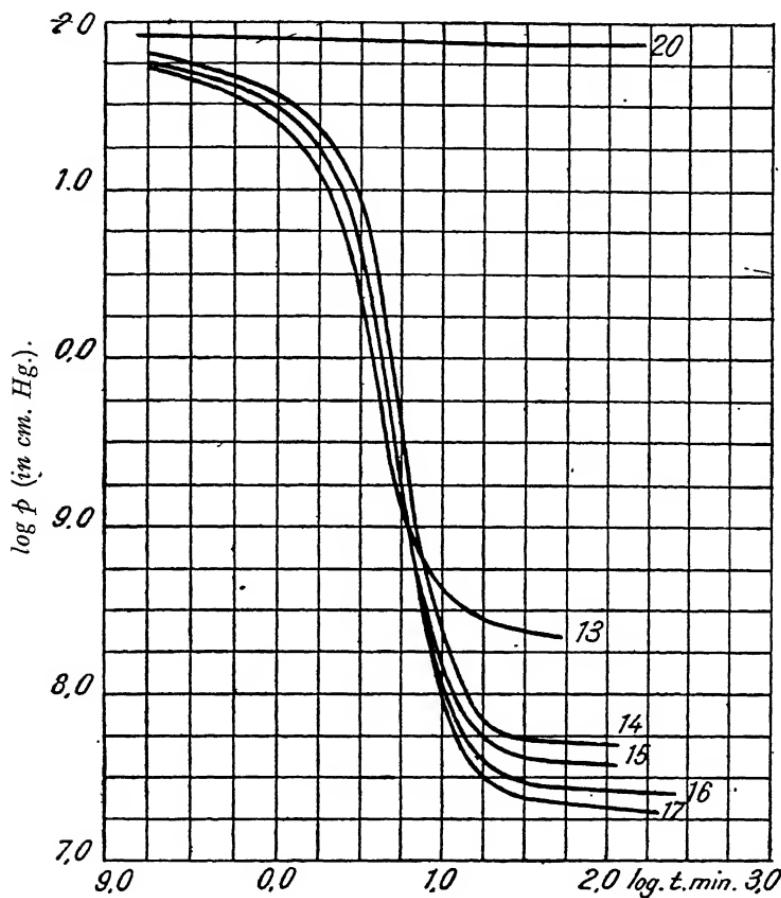
FIG. 72.

which diminishes after each treatment, except after the fourth, for which the purging was at 640°, whilst the other purgings were at much higher temperatures. Fig. 74 shows how the same sample recorded its absorbing power after prolonged heating at 650° or even lower.

Lemon, as well as other workers in this field, found that

the lower the temperature of carbonisation the greater the absorbing power. But the process of activation diminishes the interest in this point, since two samples, which were

Heat Treatment.

1. 4·5 hours at 633°.   4. 0·5 hours at 875°.
2. 0·5 ,,   ,, 800°.   5. 4·0   ,,   ,, 640°.
3. 0·5 ,,   ,, 850°.   6. 0·7   ,,   ,, 905°.
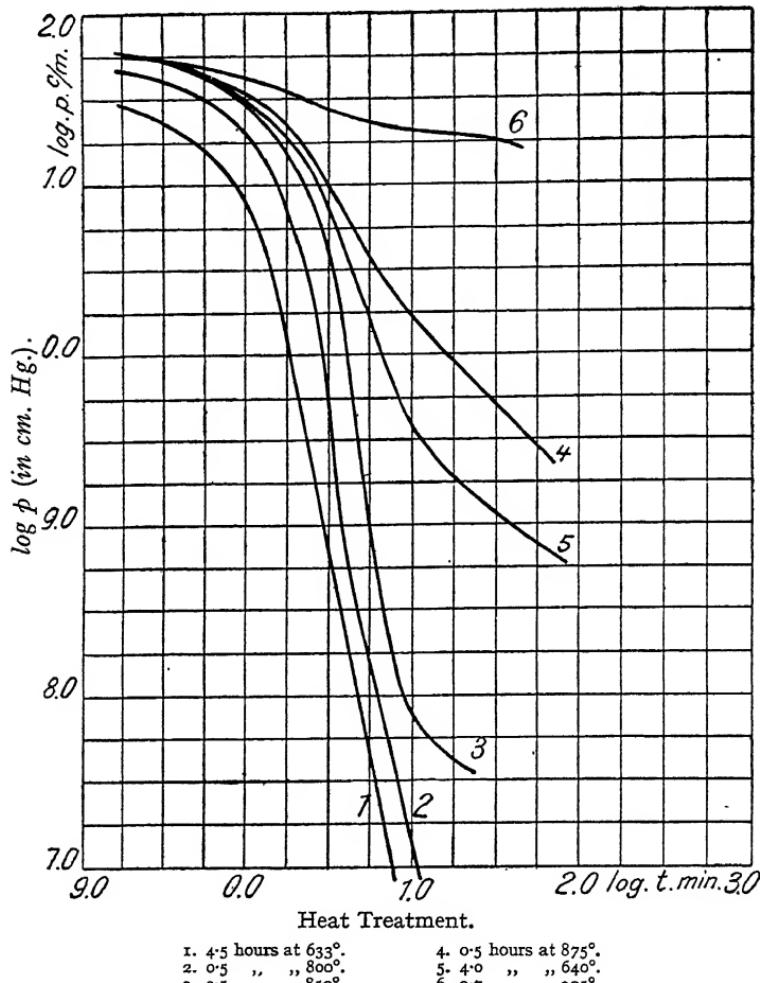
FIG. 73.

carbonised at different temperatures, can be " activated " to the same extent by subsequent treatment.

Following the idea that this activation might be due to the oxidation of non-volatile hydrocarbons, activation by

industrial methods was tried, not only for cocoanut charcoal, but for wood charcoal. One of these methods consists in passing a current of air for a long period over fine charcoal

Heat Treatment.
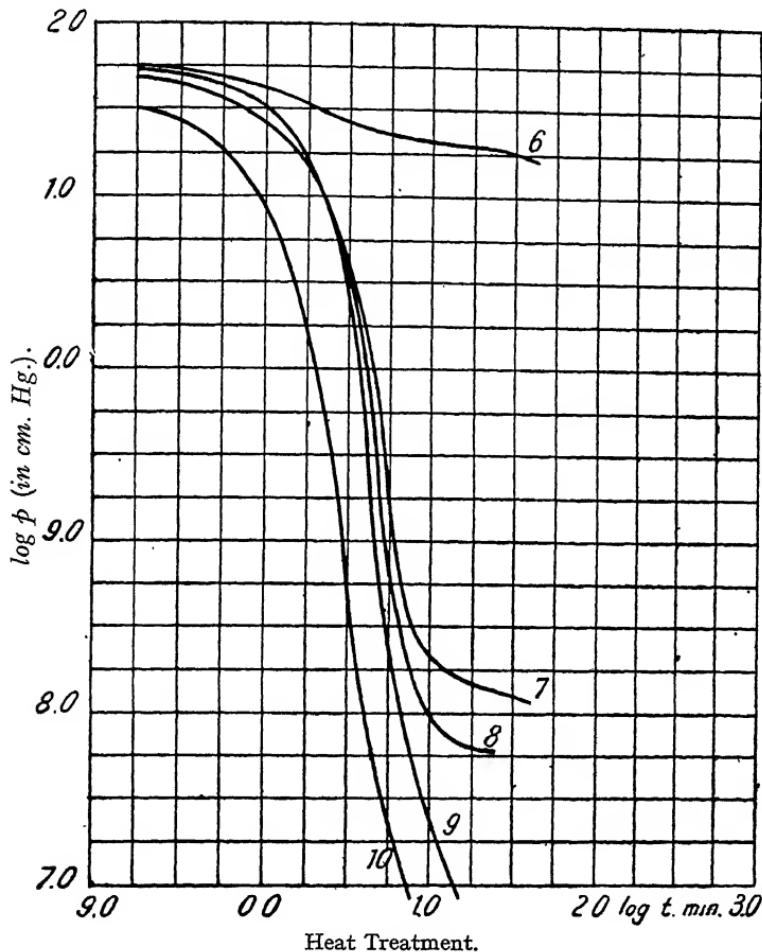
6. 0·7 hours at 905°.   9. 44·5 hours at 650°.
7. 22·0 ,,   ,, 650°.   10. 1·0   ,,   ,, 840°.
8. 22·0 ,,   ,, 500°.

FIG. 74.

screened through a sieve with from 6 to 14 meshes to the inch. The charcoal is got by carbonisation at from 850° to 900°. The air current is at a temperature between 350° and 400°.

Limiting Pressure reached and Selective Absorption. The absorption properties of wood charcoal vary with the preparation, and also with the use it has had since preparation. Thus any figure given will only indicate the order of the pressure which can be reached.

G. Claude [1] has measured the absorption of H_2, He, Ne, and N_2 by charcoal at very low temperatures and low pressures, in connection with the commercial preparation of neon. His numerical results are given in the following table, which refer to I grm. of charcoal :—

Nitrogen, $t = -183°$ C.		Hydrogen, $t = -195.4°$ C.		Neon, $t = -195.4°$ C.	
p mm. Hg.	v absorbed c.c. at atmospheric pressure.	p mm. Hg.	v absorbed c.c. at atmospheric pressure.	p mm. Hg.	v absorbed c.c. at atmospheric pressure.
0·004	9·35	0·006	0·105	0·45	0·105
0·010	18·70	0·0115	0·21	0·88	0·21
0·032	37·4	0·0205	0·42	1·30	0·32
0·088	46·6	0·036	0·84	1·74	0·42
0·385	56·0	0·083	2·05	3·50	0·84
1·107	65·3	0·176	3·71	5·30	1·22
11·50	93·0	0·475	8·40	7·20	1·63
33·2	103·0	1·060	14·0	11·30	2·44
90·0	112·0	3·50	28·0	15·5	3·25
247·0	121·0	8·7	42·0	19·4	4·06
		20·6	56·0	30·5	6·18
		43·7	63·0	40·5	8·01

It will be seen that, although neon has a higher boiling-point than hydrogen, it is much less absorbed than the latter. This fact allows us to purify the neon in lamps by absorbing the gases given off by the electrodes during the first few hours of running. Helium is less absorbable than neon (0·21 c.c. under 27 mm. of mercury).

[1] G. Claude, *Comptes rendus*, 158, 861, 1914.

The volume of gas absorbed at atmospheric pressure may be represented by an equation of the form

$$v = kp^{\frac{1}{n}},$$

in which k and n are empirical constants. If log v is plotted against log p, the graph should be a straight line, because

$$\log v = \log k + n \log p.$$

Claude's results fit in quite well with an equation of this kind. At low pressures n approaches unity—that is, the volume becomes proportional to the pressure. If this law is true for pressures below those at which Claude worked, the following table (due to Dushman [1]) gives the volumes of nitrogen and hydrogen, measured at a pressure of 1 microbar, which 1 grm. of charcoal will absorb at low temperature.

Nitrogen, $t = -183°$ C.		Hydrogen, $t = -195\cdot4°$ C.	
p in microbars.	v c.c. measured at 1 microbar and 0° C.	p in microbars.	v c.c. measured at 1 microbar and 0° C.
5·3	9,500,000	8·0	106,000
1	1,800,000	1·0	13,250
0·1	180,000	0·1	1,325
0·01	18,000	0·01	133
0·001	1,800	0·001	13

From this table, with the units used, we get $k = 1\cdot8 \times 10^6$ for nitrogen at $-183°$, and $k = 1\cdot325 \times 10^4$ for hydrogen at $-195\cdot4°$, so that we can calculate the limiting pressure which would be reached by starting from any given initial pressure.

Suppose V is the internal volume of the vacuum system, in which the pressure is p_0 before the charcoal is cooled. Let v_0 be the volume that the gas in the system would occupy under some standard conditions, say pressure $= 1$ microbar

[1] Dushman, *Gen. Elect. Rev.*, **24**, 63, 1921.

and temperature $0°$ C. When the charcoal is cooled with liquid air, absorption will go on until the pressure of the residual gas is the equilibrium pressure at liquid air temperature. Let v be the volume absorbed, measured at I microbar and $0°$ C. The amount of residual gas measured under the same conditions is $v_0 - v$. This will exert a pressure $\dfrac{(v_0 - v)}{V}$ in the system; thus the limiting pressure is given by

$$p = \frac{v_0 - v}{V} \quad \text{and} \quad v = kp^{\frac{1}{n}} \quad v_0 = Vp_0,$$

so that

$$pV = v_0 - kp^{\frac{1}{n}}$$

and if $n = 1$

$$p = \frac{v_0}{V + k} = \frac{Vp_0}{V + k}.$$

Take, for example, the case of a tube system of I litre capacity pumped out to I microbar, with a tube containing I grm. of charcoal in the system. Suppose the apparatus is sealed off from the pump and the charcoal tube dipped into liquid air. If the gas is nitrogen the limiting pressure will be given by

$$p = \frac{10^3 \times 1}{10^3 + 1\cdot 8 \times 10^6} = 0\cdot 6 \times 10^{-3} \text{ microbar.}$$

If the gas is hydrogen and the charcoal tube is immersed in liquid nitrogen, the pressure will be

$$p = \frac{10^3 \times 1}{10^3 + 1\cdot 325 \times 10^4} = 0\cdot 075 \text{ microbar.}$$

It is therefore possible to get down to very low pressures with charcoal and liquid air or liquid nitrogen, even with hydrogen in the tube system. It is worth noticing that, when the charcoal tube is being sealed off to separate it from the rest of the apparatus (of course this is done whilst the tube is still in liquid air), probably gases which come off from the hot glass will have more chance of being condensed,

and thus removed altogether, than they would in sealing off from a condensation pump, because its connecting tube will never be as short as the charcoal tube.

Daly and Dushman [1] have obtained some results which agree very well with the calculations above. They had a 3-litre bulb, with a side tube containing 5 grm. of " activated " charcoal. An ionisation gauge was also joined to the bulb, and a thin glass bulb was placed in it containing hydrogen. The apparatus was exhausted with a condensation pump, and the charcoal was heated for over an hour to 360° C. Then the pump was cut off from the bulb and the little hydrogen bulb was broken by shaking. The pressure was measured by the gauge and the charcoal tube was immersed in liquid air and the pressure read continuously. It took about an hour to attain equilibrium. The following were the results obtained :—

Volume.	Pressure after sealing off.	Initial pressure of hydrogen.	Final pressure at room temp.	Final pressure at liquid air temp.
	Microbars.	Microbars.	Microbars.	Microbars.
3025 cm³.	0·0180	0·31	0·014	0·0004
,,	0·0220	8·33	2·0	0·15
100 cm.³	0·104	8·64	0·02	0·0004
,,	9·28	17·7	0·24	0·0016

2. **Absorption by Metals.** A general account of adsorption has been given in Chapter III. The cases dealt with below are those cases of absorption by metals which are of use in improving vacua.

Absorption of Hydrogen by Palladium Black. Palladium black, or at least certain samples of palladium black, are better absorbers of hydrogen at low temperature than charcoal. The method of preparation [2] is as follows : The palladium in the form of a sheet or wire is dissolved in *aqua regia*, evaporated on a water bath until the acid vapours

[1] Dushman, *Gen. Elect. Rev.*, 24, 64, 1921.
[2] *Ibid.*, 24, 67, 1921.

have disappeared; the solution is then diluted, warmed, and a concentrated solution of sodium carbonate is added to neutralise the free acid. A slight amount of acetic acid is then added, the solution is warmed, and a warm concentrated solution of sodium formate added. The palladium comes down as a black flocculent precipitate which settles rapidly at the bottom of the beaker. The supernatant liquid is decanted and the precipitate washed with distilled water until the wash water shows no traces of chlorides. The palladium black is then washed with alcohol and then introduced while damp into a tube, and dried by blowing air over it. The palladium black is kept from blowing into other parts of the tubes by plugs of glass wool. The tube is then evacuated and sealed off. The following figures are due to Valentiner,[1] and give the equilibrium pressures and the corresponding absorbed amounts of hydrogen. These amounts are expressed in c.c. at atmospheric pressure and $0°$ C., and relate to 1 grm. of palladium.

Temp. $t = 20°$ C.		Temp. $t = -190°$ C.	
p mm. Hg.	v in c.c. under normal conditions.	p mm. Hg.	v in c.c. under normal conditions.
0·001	0·10	0·0005	2·05
0·005	0·26	0·0015	2·11
0·037	0·40	0·001	3·06
0·110	0·52	0·001	9·1
0·190	0·59	0·002	33·0
0·315	0·70	0·005	40·0
0·52	0·82	0·012	47·2
0·76	0·92	0·025	63·0

These results show that the absorbing power at the temperature of liquid air is much greater than that of charcoal, but also (3 and 9 c.c. for the same pressure 1μ) that the absorb-

[1] Valentiner, *Verh. d. deutsch. Physik. Ges.*, 3, 1003, 1911; also Dushman, *loc. cit.*

ing power is not very definite. As a matter of fact, certain specimens made in the laboratory of the American General Electric Co. did not absorb at all, for no known reason.

This erratic behaviour makes its use a doubtful advantage, but active specimens are very useful. Dushman gives the following example of its use: " An ordinary lamp exhaust system was used, giving an exhaust pressure of about 1 microbar. A few milligrams of palladium black were placed in a kenotron (about 100 c.c. volume)." The tube was exhausted with the oil pump with simultaneous heating for over thirty minutes to 300° C., and sealed off. The metal cylinder was then bombarded to a white heat by electrons from the filament in order to liberate occluded gases. These were absorbed so completely by the palladium black that the space charge characteristics obtained for the valve corresponded to a pressure 0·05 microbar. Similar results were obtained time after time.

Absorption of Gases by the Alkaline Earth Metals and Rare Earth Metals. It has been known for many years [1] that the metals of the alkaline earth group, calcium, strontium, and barium, combine with nitrogen to form nitrides. A large amount of heat is given off by the reaction, but it is difficult to start the combination. This fact is explained by some interesting results due to Soddy,[2] who showed that the reaction takes place readily if the metal is in the vapour state. Similar combinations take place between these metals and the gases of the zero group, as well as nitrogen. It would seem that this property might be used as much in vacuum work as in the preparation of these gases, but up to the present it has hardly been used at all in low-pressure work. No figures are available regarding the dissociation pressures of the products obtained and the limiting pressure reached. The vapour pressures of the metals themselves would cause no trouble, because calcium at 500° C. has a vapour pressure only 0·5μ.[3] It rises rapidly above this temperature and reaches 173μ at 700°.

[1] Moissan, *Comptes rendus*, **127**, 497, 1898.

[2] F. Soddy, *Proc. Roy. Soc.*, **78**, 429, 1907.

[3] Norman Pilling, *Phys. Rev.*, **18**, 362, 1921.

The affinity of the rare earth metals for nitrogen has also been known for a long time. Cerium and thorium absorb nitrogen and become incandescent when they are heated to below redness.[1] Zirconium [2] also does this. The vapour pressures of these metals are not known, but they are certainly small. Coolidge [3] has suggested an interesting method based on the use of these metals, when a vacuum is needed so high that no gas ionisation effects can be observed when an electron current is transmitted. The apparatus is evacuated in the ordinary way, and the glass parts are warmed and the metal parts raised to red heat whilst pumping is going on. Then air or dry nitrogen is introduced, and a little cerium or thorium in the form of a fine powder is introduced through a small side tube which is then sealed off. The pump is then started again and the apparatus is then sealed off from the pump. The powdered metal is then heated. The metal is observed to glow as a reaction takes place. The pressure attained is low enough to be suitable for a hot cathode device.

Disappearance of Gases, at Very Low Pressures, in the Presence of an Incandescent Tungsten Filament. In a series of investigations on the emission of tungsten and molybdenum filaments, Langmuir observed remarkable peculiarities in certain chemical reactions at pressures which were so low that the number of gas molecules colliding with other gas molecules was small compared with the number which, after striking the incandescent filament, pass directly to the walls of the bulb and remain there permanently in some cases, and in some cases subsequently evaporate. These reactions are not only interesting in themselves, but also interesting from the point of view of the effect on the lamp. Lack of space prevents a full description of these reactions being given here. They have never been used to improve vacua, since they take place at relatively high pressures. According to Langmuir,[4] oxygen does not react with tungsten below 0·001 microbar,

[1] Matignon, *Comptes rendus*, 131, 891, 1900; Matignon and Delépine, *ibid.*, 131, 837, 1900.

[2] Mallet, *Amer. J. Sci.*, 28, 346, 1859.

[3] Coolidge, Patent No. 1,323,386, 2nd December 1919.

[4] Langmuir, *J. Amer. Chem. Soc.*, 37, 1139, 1915.

although it stops the blackening of the bulb due to evaporation of the metal, and also reduces the electron emission to a fraction of its normal value. With nitrogen, tungsten behaves like the alkaline earths, and only reacts when the tungsten is vaporised. The rate of disappearance of the nitrogen is proportional to the product of rate of evaporation of the filament and the pressure of the nitrogen ; thus the rate of disappearance increases very rapidly with the filament temperature (above 2700° Abs.), but for a given temperature of the filament the pressure of the residual nitrogen is an exponential function of the time, and the rate gets slower and slower. Tungsten vapour also combines with carbon monoxide. Langmuir has mentioned these reactions often in support of his theories of chemical combination, but he does not give any figures for the pressures below which nitrogen and carbon monoxide will not react with tungsten vapour. All the figures which he gives relate to pressures which are at least several microns of mercury. But the use of electric discharges in conjunction with the filament affords a better method of cleaning up residual gases.

Since mercury condensation pumps are in general use for reaching very low pressures, the following observations of Hughes and Pointdexter [1] will be very useful to workers to whom a supply of liquid air is not available :—

" The alkali metals have an extraordinary power for absorbing mercury vapour, and may, therefore, be used as a mercury trap in place of liquid air. Our practice is to put a small piece of sodium or potassium (a gramme is ample) into a trap between the diffusion pump and the apparatus to be exhausted, and to distil it, after the vacuum has been obtained, on to the sides of the trap, thus lining it with the metal for a few centimetres. The trap may be of the usual liquid air type, or it may be merely a bent tube with the metallic lining of distilled metal distributed over the inner surface at or near the bend.

" Using an ionisation gauge for the vessel to be exhausted, we have found that the pressure of mercury vapour in it, with a potassium-lined trap between it and the pump, is

[1] Hughes and Pointdexter, *Nature*, 15, 979, 1925.

certainly less than 5×10^{-9} mm. We have made direct comparisons between the trapping power of a potassium-lined tube and that of the usual liquid air trap, the same ionisation gauge measuring the pressure reduction. We have found that the potassium-lined trap is quite as satisfactory as liquid air. The residual pressures obtained in various tests seem to depend entirely upon the vigour with which the ionisation gauge and connecting tubes were outgassed by heat treatment before the measures were made, and not at all upon whether liquid air or metallic potassium is used to trap the mercury. We are convinced that the lowest pressure obtained, namely, 5×10^{-9} mm., is partly, and possibly nearly all, due to residual gases, owing to insufficient heat treatment, and that the figure is merely an upper limit to the vapour pressure of mercury in a vacuum system beyond a potassium-lined trap.

"The passage of several litres of moderately dry air at atmospheric pressure over the potassium has no serious effect on its power to trap mercury vapour, although one might well have feared such would be the case from the discoloration of the surface produced by the air.

"From a practical point of view, it is of importance to know how long the alkali metals retain their power to act as a mercury vapour barrier. In one test, in which sodium was the active metal, the pressure in the ionisation gauge beyond the trap after twenty-five days was within 50 per cent. of its initial value (2×10^{-7} mm.). We do not know whether to attribute this slight pressure increase to loss of absorbing power by the metal, or to a gradual evolution of gas.

"In a second test we have used the first appearance of mercury lines in the spectrum of helium, at less than $0 \cdot 01$ mm. pressure, as a criterion of the diminution of trapping power of a potassium-lined trap for mercury vapour. The mercury lines did not appear until the eleventh week, in which time the potassium had absorbed a little more than 150 per cent. of its own weight of mercury."

3. **Disappearance of Gases during Electrical Discharge with and without Absorbers.** *Discharge without Absorbers.* It is well known that ordinary X-ray tubes harden when a discharge

is passed for some time—that is, the gas pressure diminishes, so that various " softening " devices have been put into the tubes. Although many experiments were made on the effect, no definite information was got from work with high potentials and cold cathodes. But a great deal of precise information has been got from experiments on incandescent lamps and thermionic valves, and the phenomenon has been, to a large extent, explained. Most of the work was done in the laboratories of the English General Electric Co. and the American General Electric Co., with the idea of cutting down the cost of production of lamps as far as possible, and in order to facilitate mass production.

Figures have been given in Chapter III for the time necessary for the elimination of occluded gases by heat treatment *in vacuo*, but in lamp factories the process of evacuation cannot be continued for such long periods. Although it is admitted that the life of a " monowatt " lamp depends on the pressure in the lamp, and is much longer for lower pressures, the lamps are joined to a vacuum system in which the pressure is rarely below 1μ, and are only pumped out for about a quarter of an hour, whilst the temperature to which they are raised is 300° at most. When the fact that the lamp is joined to the vacuum system by a capillary tube is taken into account, and also that the heating starts at room temperature, it will be seen that the final pressure in the bulbs must be fairly high. According to Dushman,[1] they do things still quicker in America, and the lamps are only on the evacuation rack for from five minutes to half a minute.

Thus, after sealing off, the pressure of the residual gases in the lamp may be anything from 1μ to 100μ, so that some way of cleaning up the residual gases is essential.

In order to do this the lamps are " aged " whilst they are being tested. They are run at a fixed voltage higher than that for normal running. During the first few minutes of running the lamps are filled with a blue glow, which diminishes in intensity and finally disappears. This blue glow is due to ionisation of the residual gases by the electrons which come

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[1] Dushman, *Gen. Elect. Rev.*, 34, 676, 1921.

off from the filament, and are accelerated by the electrostatic field between the ends of the filament.   The glow is accompanied by the disappearance of gas.   Dushman and Huthsteiner's results on this effect are shown by the curves of fig. 75.

The curves show the diminution in pressure in a 100-watt 120-volt lamp, filled with air.   For curve A the initial pressure
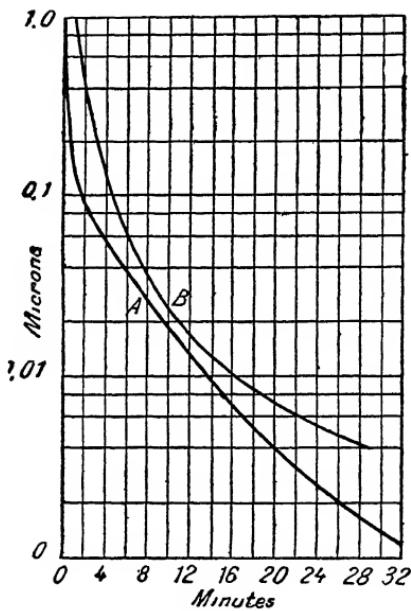
FIG. 75.

was 1μ, and for B, 5μ.   An ionisation gauge was fused on to the lamp in order to measure the pressure.   Before the air was introduced the lamp and gauge were well exhausted by baking for an hour at 360° C., and flashing the filaments to a high temperature whilst the pumping was going on.   The voltage used in the cleaning up was 156—that is, 130 per cent. of the normal working voltage.   The blue glow disappeared in a fraction of a minute, and most of the gas was cleaned up during this period.   After this the rate of pressure decrease grew smaller continuously.   After about a quarter of an hour the pressure was of the order of $0·01\mu$.

The Employment of Phosphorus as an Absorber. In 1894 Malignani suggested the use of phosphorus for cleaning up residual gases after sealing. In about a minute a small quantity of phosphorus will clean up about 90 per cent. of these gases. This is shown in fig. 76, which also relates to a monowatt lamp of 100 c.p., 120 volts, overvolted as in the previous cases. Curve A is for initial air pressure 10μ, and B
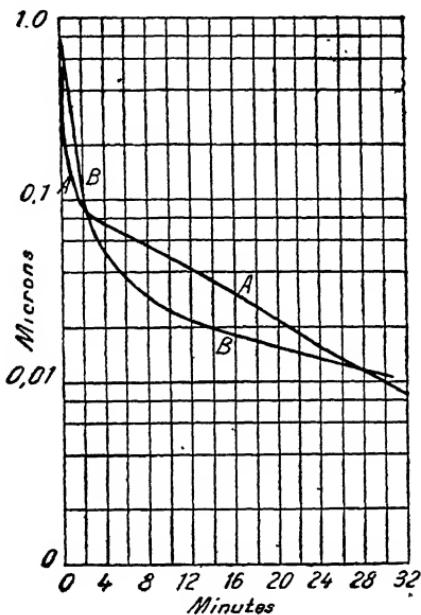
FIG. 76.

for 5μ. The lamp and gauge were exhausted and baked as before, and then the lamp was removed from the pump and a few drops of a suspension of red phosphorus in alcohol were painted on the leads just below the filament. The combination was then reassembled, exhausted, and baked at 360° C. for five minutes, and then sealed off. Whitney [1] has shown that similar results can be got with arsenic, sulphur, and iodine. Arsenic is used for this purpose in Cooper-Hewitt mercury vapour lamps for alternating currents, and also in other lamps.

[1] Whitney, *Trans. Amer. Inst. Elect. Eng.*, 31, 921, 1912.

Fig. 77 is also due to Dushman and Huthsteiner, and shows the separate effects of clean up by discharge and by phosphorus. The lamp used contained two independent filaments, and was joined to an ionisation gauge as in the other experiments. Curve A shows the drop of pressure due to one filament alone being raised to incandescence and without the use of phosphorus. The only electrostatic field in this
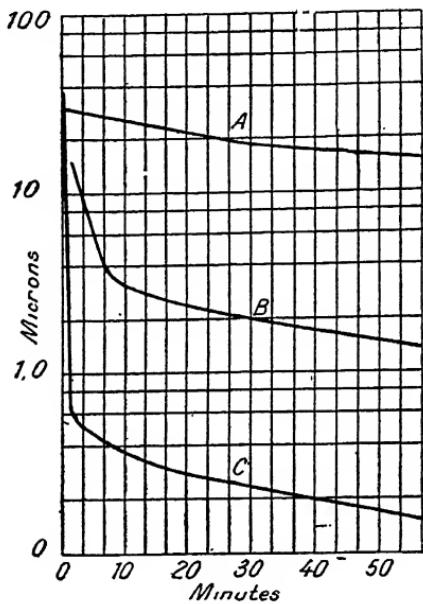
FIG. 77.

case is between the ends of the incandescent filament. Curve B is got by using the second filament as anode and raising it to 250 volts. Curve C shows the " clean up " due to red phosphorus on the leads of the cathode filament and 250 volts on the anode filament. The drop shown in C is much more rapid than that in B.

There are several methods for introducing phosphorus into lamps. Campbell, in work which will be described later, sometimes introduces the vapour from white phosphorus, and sometimes uses red phosphorus. In the first case the white phosphorus is contained in a little side tube which is

cut off from the lamp bulb by means of a tap, which is only opened during the short time required for the vapour to diffuse into the bulb. If the tap were left open the vapour would penetrate throughout the vacuum system and leave deposits of red phosphorus. The amount of phosphorus introduced can be calculated from the vapour pressure. The most recent measurements of the vapour pressure of white phosphorus are due to McRae and Van Voorhis,[1] the range throughout which they determined the pressure being from 44° to 150° C. They agree very well with the results of Jolibois [2] for the range 144° to 315° C. By extrapolation of the first set the following table of pressures is obtained :—

Temp. °C.	0	10	20	30	40	50	60	70	80	90	100
Vap. press. of white phosphorus, μ.	7	16	35	71	139	262	472	823	1390	2280	3630

To use red phosphorus a suspension of the phosphorus in the form of a very fine powder is made in alcohol or even water. A little sodium silicate is added to make it stick better. The suspension can be used in several ways : one way is to drop a little on the filament holder ; but a better way is to dip the filament in it, so that the phosphorus is volatilised when the filament is heated.

With the latter method certain salts, particularly fluorides, have been introduced into the suspension, and are found to improve the clean up. This point will be referred to later.

4. **The Study of Electrical Clean Up.** A great deal of work on the disappearance of gas in the electric discharge has been done by Campbell and his collaborators.[3] A large number of interesting results have been obtained, but these do not always agree with one another, and the interpretation is very uncertain. The method and the principal results are given below.

The bulb L (fig. 78) contains a tungsten filament F, which

[1] McRae and Van Voorhis, *J. Amer. Chem. Soc.*, 43, 547, 1921.

[2] Jolibois, *Comptes rendus*, 149, 287, 1909 ; and 151, 382, 1910.

[3] Research Staff of Gen. Elect. Co., London, *Phil. Mag.*, 40, 585, 1920 ; 41, 685, 1921 ; 42, 227, 1921 ; 43, 914, 1922.

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will take a current of $1\cdot4$ amperes at 10 volts. The supports of the filament were of nickel wire $0\cdot6$ mm. in diameter. A similar piece of nickel wire N served as the anode. The filament current was furnished by the battery B and regulated by the variable resistance R_1, the ammeter A_1, and the voltmeter V_1. Any desired potential difference between the filament and the anode could be established by means of the 600-volt dynamo D acting through a potential divider R with a fine adjustment. The potential between the anode
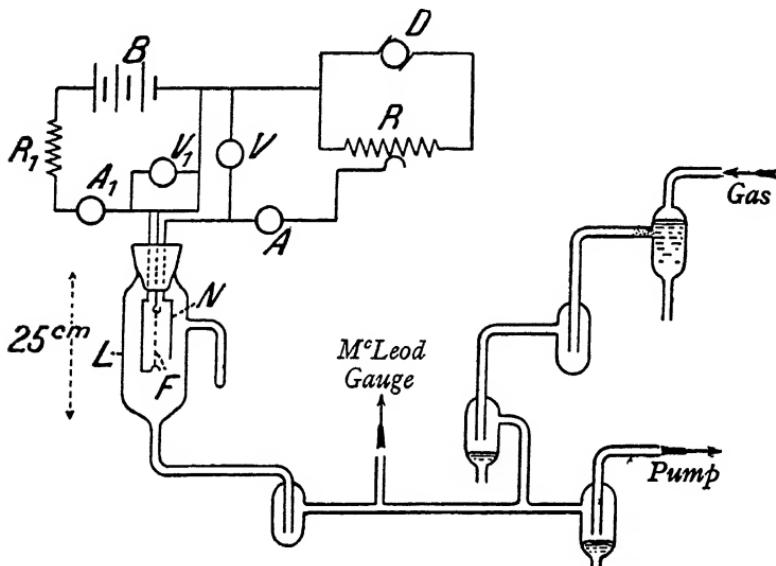
FIG. 78.

and the negative end of the filament (V) was measured by the voltmeter V reading to $0\cdot1$ volt; the current (i) between the electrodes was measured by the shunted microammeter A. By manipulation of the mercury cut-offs and the liquid air traps the experimental bulb could be evacuated, and then small quantities of gas could be let in. The pressures were measured with a McLeod gauge and not with an ionisation gauge. The pressures mentioned by Campbell are all much higher than those met with in the work done by the various American workers: as a rule they are higher than 1μ.

The bulb shown in fig. 78 was used to study the action

of the discharge without phosphorus, and also with white phosphorus vapour introduced through a tap from a small side tube. In studying the effect of larger quantities of phosphorus, a paste of red phosphorus was deposited on the filament of a lamp which had no anode. This filament was so long (1 metre of wire of 0·026 mm. diameter) that the electrostatic field between its ends was fairly big ; in this case the pressures were measured by using the lamp itself as a Pirani gauge.

Relation between the Disappearance of Gas, the Glow, and
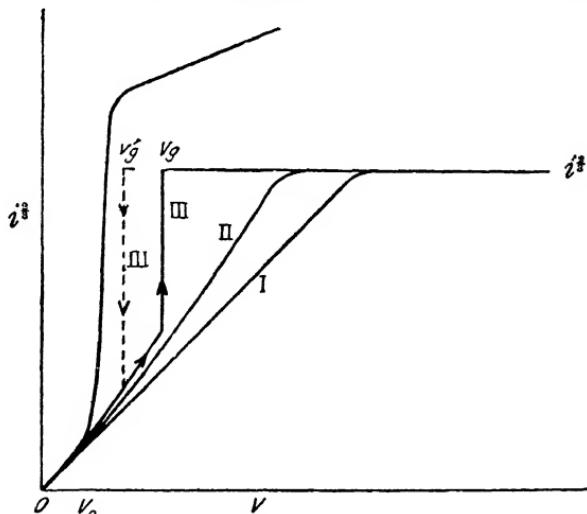
FIG. 79.

the Ionisation. Influence of the Nature of the Gas. With the bulb shown in fig. 78, if the vessel is highly evacuated (pressure less than 1μ) the current i, between the filament and the anode, is independent within wide limits of the temperature and the thermionic emission of the filament, and, so long as V is below a certain limit, varies simply as $V^{\frac{3}{2}}$. If V is increased sufficiently, the current becomes saturated and reaches a value (i_0), determined wholly by the thermionic emission. The relation between i and V in this condition is shown by curve I in fig. 79, in which $i^{\frac{2}{3}}$ is plotted against V.

If a little gas is present (at a pressure about 1μ for example),

curve II is obtained. " It leaves curve I at the ionisation potential of the gas (V_0), and attains the same value of the saturation current at a value of V less than before. The saturation current is the same, because the current conveyed by the ions formed in the gas is an inappreciable fraction of the total current." No glow is seen even at 600 volts. If there is a little more gas (pressure about 2μ), curve III is obtained, the current now rising sharply to the saturation value. The sudden increase in the current corresponds to the appearance of glow in the tube. The potential at which this sudden rise takes place (V_g) is called by Campbell the glow potential. According to Campbell this is quite distinct from the ionisation potential, and depends on the disposition of the electrodes and the dimensions of the bulb.

The change is discontinuous, and this is shown by the fact that if the changes in V are reversed the curve is not repeated downwards, and the curve III represents the changes in current. The potential can be lowered from V_g to V_g', and the current will still have its saturation value. When the potential reaches V_g' the current falls rapidly, and for slightly lower values the curve joins curve III. According to Campbell's earlier papers the discontinuity is of considerable importance in the disappearance of gas.

If there is still more gas (pressure of the order 50μ), the discontinuities are not so marked. The ionisation current is no longer negligible compared with the electron current, and curve IV shows the variation of $i^{\frac{1}{2}}$ with increasing V. The glow in this case is usually fainter and more difficult to see than is the glow corresponding to curve III.

The following table gives the glow potentials of various gases at a pressure about 5μ. It will be noticed that the glow potential for hydrogen is affected to a very large extent by the least trace of a gas of high molecular weight. Similarly, mercury vapour at ordinary temperature suppresses the nitrogen spectrum in the glow, and mercury lines are still visible in the nitrogen glow when the mercury from which the vapour comes is at $-78°$ C. (which shows that solid carbon dioxide will not completely condense mercury vapour, at any rate in a short time).

Gas.	V_g.
A	40 volts
CO	58 ,,
N_2	62 ,,
H_2 (pure) . . .	> 200 ,,
H_2 (with traces of wax vapour)	165 ,,
H_2 (99 per cent.)	90 ,,

The difference between V_g and V_g', which Campbell calls the rising and falling glow potentials, is very interesting with regard to the clean up of residual gases by electric discharge in practice. Fig. 80 shows the values of V_g and V_g' for argon plotted against the pressure (in mm. Hg.). Suppose the initial pressure corresponds to the value ON, and suppose that the anode potential is gradually raised. The glow appears suddenly when the potential reaches the value NA. Gas disappears rapidly at constant voltage, the change being represented by AB. At B the falling glow potential (V_g') curve is reached, and the rate of disappearance slows down considerably and the glow stops. If the potential is now raised continuously the point C on the (V_g) curve will be reached, and the glow will reappear with rapid absorption of gas. The path followed will be CD. The process can then be continued through DE, and so on. From this it will be seen that if, during the making of a lamp, a high voltage dangerous to the filament is not to be applied, it is better to start the " clean up " by discharge at pressures which are not too low. Suppose, for example, the highest safe voltage during evacuation is the ordinate of C in fig. 80, but that in later working the filament should stand a voltage represented by the ordinate at E. If the treatment is begun at the state represented by C, the glow will reduce the pressure to D, and the tube will stand the voltage at E without glowing. On the other hand, if the initial pressure were lower than that at C, the applied potential (less than or even equal to that at C) would not have started the glow and lowered the pressure; thus if the voltage corresponding to E were afterwards applied, the lamp would glow.

It is seen that the disappearance of gas is bound up with
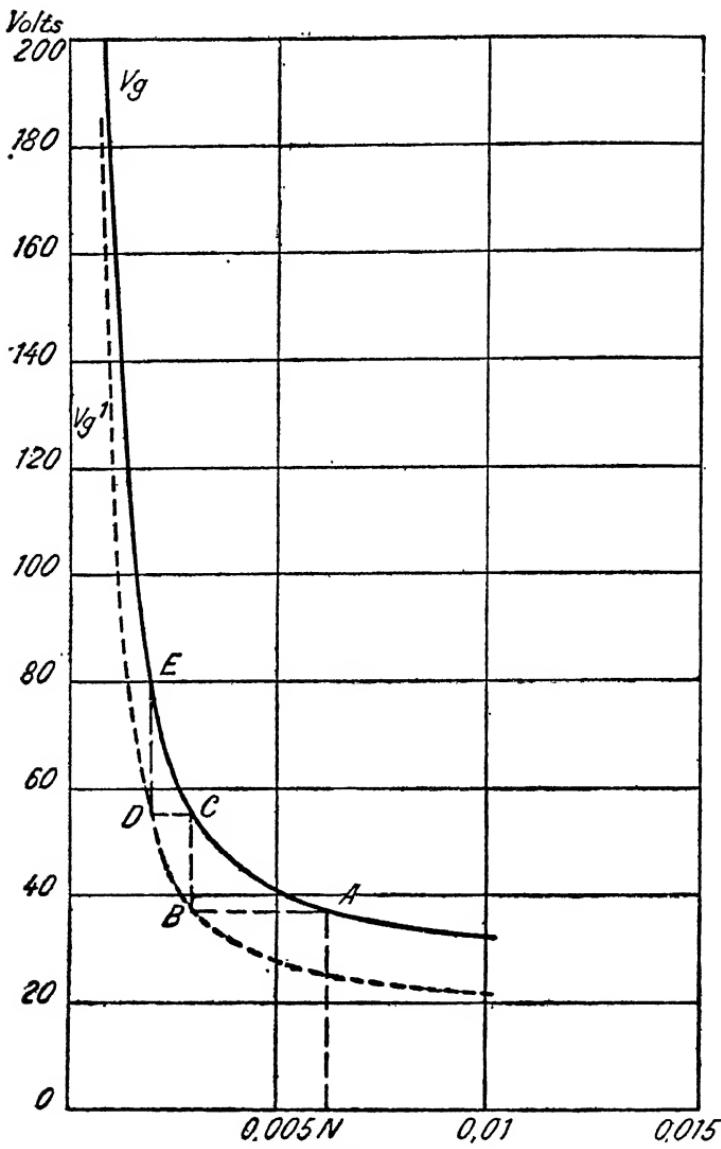
FIG. 80

the glow. In his first papers, Campbell even went so far as
to state that, if the gas current was not accompanied by the

glow (due to low voltage or low pressure), no gas disappeared. In order to explain this phenomenon it was important to find out the relation between the glow and the ionisation of the gas. This work presented many difficulties. Campbell's third paper deals mainly with this point. The variation of i as the voltage is increased is not quite as simple as that shown in fig. 79. Just before the glow potential V_g is reached the current is a little greater than when the glow begins. This might be thought to show that the ionisation is less when the gas glows, but, as a matter of fact, the ionisation increases considerably when the glow starts. The apparent anomaly is due to the fact that the walls of the bulb act as an extra electrode and collect the greater part of the ions formed. This leads to the supposition that the disappearance of the gas is due, in part at any rate, to ionisation and subsequent collecting of the gaseous ions by the walls of the tube. But no definite data have been obtained up to the present about the relation between the rate at which ions are formed and the rate of disappearance of gas.

The general characteristics of the phenomenon are the same for all gases, but there are many singularities which are very difficult to explain. Some gases give rise to chemical reactions or decompose, with the production of substances which are easily condensed or absorbed. Thus carbon monoxide suffers the transformation

$$2CO = C + CO_2,$$
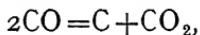
which seems rather extraordinary, but Campbell seems to have established this beyond doubt. It is due to collision between a neutral CO molecule and a CO ion. With regard to the gaseous elements, hydrogen causes complications due probably to the formation of atomic hydrogen by contact with incandescent tungsten. Atomic hydrogen is very easily taken up by the walls of the vessel. Mercury vapour seems to be able to liberate an indefinitely large amount of hydrogen from the walls of the tube, even though they have been well purged beforehand. The results for nitrogen are more definite, but there are still some doubtful points about its behaviour. Langmuir holds that a solid compound WN_2 is

formed, which produces ammonia when damp air is let in to the bulb. Campbell denies the existence of this compound in the tubes. The disappearance of argon is also irregular, but always slower than the rate for other gases.

Pure phosphorus vapour disappears much more quickly than the gases mentioned above. Campbell used the apparatus of fig. 78 to study its action. A side tube containing white phosphorus was attached to the lamp and separated from it by a tap. The lamp was also separated by a tap from the rest of the apparatus. By exhausting with both taps open, and first closing the tap between the lamp and the pump, and then later the tap to the phosphorus tube, the lamp could be filled with phosphorus vapour at a pressure corresponding to room temperature, or, by cooling the side tube, at a pressure corresponding to any lower temperature. When the filament was raised to 2500 Abs. (the bulb being at room temperature), the vapour seemed inactive ; but when the potential of the anode was gradually raised, a definite glow potential was reached at 46·5 volts with the bulb at 17° ·C., and at 58 volts with the bulb at 0° C. The glow had a characteristic blue colour, probably due to carbon compounds from the tap grease ; but it only lasted a second or two. At the moment that the glow discharge passed a yellow deposit appeared on the bulb (this " yellow bulb " is quite familiar to lamp makers). If the vapour is renewed several times and the process repeated, the deposit on the walls becomes thicker and deepens to brown in colour. This is almost certainly a deposit of red phosphorus, which has a negligible vapour pressure at ordinary temperatures.

Another peculiarity of phosphorus vapour is the big difference between the rising and falling glow potentials (V_g) and (V_g'). It is difficult to get exact measurements of these owing to the short duration of the glow. " An indication is obtained by observing by what amounts the potential must be raised in order to start the discharge once more, when it has ceased owing to the disappearance of the vapour (*i.e.* by tracing out the line $NABCDE$ of fig. 80). This amount is the difference between V_g and V_g' at the same pressure. If in argon we start with a glow potential of 38 volts, the

successive values of V requisite to start the discharge when it has stopped will be 38, 54, 76, 105, 15 . .   In phosphorus vapour, the successive values are approximately 46·5, 78, 350.

If, instead of evacuating the bulb before the phosphorus vapour is let in, a definite amount of gas is left in at a pressure below a definite limit (about 40μ), the glow phenomena do not seem to be very much affected by the presence of the phosphorus, but gas disappeared far more rapidly than when there was no phosphorus, except possibly in the case of argon, and much lower pressures were reached : for example, $0·2\mu$ instead of 10μ ; the pressure continues to fall very slowly after the initial period of rapid absorption.   By introducing fresh charges of phosphorus vapour, unlimited quantities of gas could be made to disappear, and at the same time the brown deposit grew thicker, which showed that the walls of the bulb play a large part in the action.

The Influence of the Walls of the Vessel.   The Effect of Certain Salts.   Further experiments brought out even more markedly the effect of the walls of the vessel.

The amount of gas which disappears in the presence of a given weight of phosphorus is greater in a lamp with a big bulb, in which the surface exposed to the discharge is large, than in a smaller bulb joined up to the vacuum apparatus by a narrow tube, in order to have the same total volume as that in the first case.

This leads to the conclusion that the state of the walls of the vessel influences the disappearance of the gas.   The experiments which Campbell made to confirm this have a great theoretical and practical interest.   A bulb was used first of all without clearing the walls of surface gases, and the absorption was found to be small and irregular.   The bulb was then pumped out and heated to 450° for five minutes. This did not clear off all the surface gases, but it was sufficient to make the absorption far more regular.   The absorption is, however, within wide limits, independent of the state or nature of the surface.   Silica and different kinds of glass did not differ in this respect, and treatment of surfaces, such as washing with acids and alkalis, and etching with hydrofluoric acid, grinding with sand and silvering chemically,

did not affect absorption, which is not even changed by depositing salts on the walls by the evaporation of solutions.

If salts are deposited on the filament they materially affect absorption. When the filament is raised to incandescence, after heating the bulb and evacuating as before, the salts are vaporised and thrown off on to the walls of the bulb. No doubt this is accompanied by ionisation of the salt, shown by a glow which occurs when the filament is raised to incandescence, and also by the fact that there is a measurable current between the filament and the anode, even with a difference of potential of 10 volts. The glow is also accompanied by disappearance of gas, as with phosphorus. If phosphorus vapour is introduced after the salt has been vaporised, or if the salt was originally mixed with red phosphorus, as indicated above, the amount of gas absorbed in the presence of a given mass of phosphorus is very much increased. The salts which are active in this way are the chlorides and fluorides of sodium and lithium, and also the silicates. Oxides and the potassium halides have no effect. Sulphates and some other salts could not be tried, because they attack the filament. The following figures give some indication of the effect of NaF with a constant quantity (0·05 mg.) of phosphorus. It will be noticed that the absorption rises quickly when the mass of salt passes a certain definite value (about 0·3 mg.). This would correspond to a layer 3 molecules thick on the walls of the bulb.

Weight of NaF on filament in mgm.	0	0·09	0·2	0·28	0·36	2·0
Hydrogen absorbed (in mgm.)	0·0007	0·0007	0·0007	0·0019	0·0023	0·002

A similar effect can be got by the sputtering of the filament. A large number of observations, both with and without phosphorus, showed that this was accompanied by the rapid disappearance of gas. This sputtering quickly blackens the bulb.

Recovery of the Gases. An Attempt at Explanation of the Phenomenon. All the cases of absorption described above are due to the fact that a vapour, probably ionised, forms a solid deposit by condensing on the walls of the bulb, and

does not evaporate again owing to the low temperature of the walls, or, in the case of phosphorus, to the formation of an allotropic modification which has a very low vapour pressure. This explanation seems almost too simple, but it leads us to think that the gaseous molecules are simply imprisoned in a deposit of non-volatile solid, which may be formed, as in the case of the fresh charges of phosphorus vapour, of any number of layers, each layer giving a fresh surface for holding the molecules of gas. The part played by ionisation in this process is probably that, instead of the gaseous molecules being simply embedded in the solid deposit, they are held there by electrostatic forces. A layer of phosphorus or of salt and a layer of gas will form a double layer with no external field.

If this theory is correct there will be no definite formation of chemical compounds. To test this Campbell analysed the residual gases by the method which has already been described. Except for gases which were deliberately introduced, no gases other than H_2O, CO, CO_2, and traces of PH_3 and NH_3, were found in any analysis. Since the dew-point of all these gases is above the temperature of liquid air, they could be detected if their partial pressures were not less than 0.5μ in the presence of 100μ of non-condensable gas. Thus it seems unnecessary to suppose that certain extraordinary chemical compounds are formed, in order to explain the phenomenon.

But if the gas is really embedded in the surface deposits it should be possible to recover it. This verification is difficult experimentally, because H_2O and CO_2 are given off in almost unlimited quantities from glass when it is raised to a high temperature. Thus a comparison bulb which has not been " cleaned up " must be used and heated under the same conditions. Campbell obtained the following results :—

At room temperature the gas is apparently permanently absorbed. Treated bulbs were kept for a year and then tested. The most delicate experiments showed no sign of liberation of gas. When absorption takes place in the presence of phosphorus, heating the bulb to between $100°$ and $120°$ C. liberates a small amount of gas, but this is taken

up again on cooling. When the temperature is raised to about 180°, an irreversible liberation takes place, but the rate of liberation only becomes rapid at 300°; at 350° all the gas comes off in a few seconds, and it is always accompanied by phosphorus vapour. If the absorption took place in the presence of salt evaporated from the filament, the amount of gas which could be liberated was much less; in some cases no gas was given off even when the glass was heated until it softened.

The above results were only obtained with nitrogen. When the bulb was warmed in order to get back the absorbed gas hydrogen, water and carbon dioxide were always given off, even when the bulb initially contained only nitrogen. When the bulb was originally filled with hydrogen it was difficult to compare the amount liberated with the amount absorbed.

The bulk of the experimental facts agree quite well with the theory given by Campbell. Nevertheless, in spite of the large amount of work which has already been done on the point, more work is needed before we can fully explain the disappearance of gas, particularly in the case which is apparently most simple—that of electric discharge without an absorber.

BIBLIOGRAPHY

THIS bibliography is not intended to be exhaustive. It is a list of publications known to the author and regarded as important in giving useful information about either apparatus or physical processes. Some of the papers given here are not mentioned in the text of this book, owing to lack of space to give them adequate treatment, although they deal with questions of great importance in vacuum technique.

I.—PUMPS

VON REDEN. *Phys. Zeits.*, **10**, 316, 1909.
GERMANN and E. CARDOSO. *J. Chim. Phys.*, **10**, 306–309, 1912.
SCHEEL and HEUSE. *Zeits. f. Instrumentenkunde*, **29**, 47, 1909.
PAMFIL. *J. Chim. Phys.*, **11**, 801–804, 1913.
WINKELMANN. *Handb. d. Phys.*, **1**, **2**, 1314–1332.
ENCYCLOP. BRITAN. 11th ed., **22**, 646.
GUICHARD. *Bullet. Scient. trimestriel.*, **3**, 1911.
E.-H. BARTON. *An Introduction to the Mechanics of Fluids*, p. 197, 1915.
GAEDE. *Phys. Zeits.*, **14**, 1238, 1913.
—— *Verh. d. deutsch. Phys. Gesel.*, **7**, 287, 1905, and **9**, 639, 1907.
—— *Phys. Zeits.*, **6**, 758–760, 1905, and **8**, 852, 1907 (Mercury Pump).
MEYER. *Verh. d. deutsch. Phys. Gesel.*, **10**, 753, 1907.
FISCHER. *Verh. d. deutsch. Phys. Gesel.*, **7**, 383, 1905.
GAEDE. *Phys. Zeits.*, **13**, 867–870, 1912, and *Ann. d. Phys.*, **41**, 337–380, 1913 (Molecular Pump).
GOES. *Phys. Zeits.*, **13**, 1105, 1913, and **14**, 170, 1913.
L. DUNOYER. *Bulletin de la Soc. fr. de Phys.*, p. 100, 1912.
F. HOLWECK. *J. de Phys.*, **3**, 645, 1922, and *Revue d'Optique*, **1**, 274, 1922 (Molecular Pump).
MAURICE LEBLANC. *Bulletin de la Soc. d'Encouragement*, Dec. 1911.
GAEDE. *Ann. d. Phys.*, **46**, 357–392, 1915 (Diffusion Pump).
A. B. WILLIAMS. *Phys. Rev.*, **7**, 583, 1916 (Condensation Pump).
HELEN HOSNER. *Gen. Elect. Rev.*, **19**, 316, 1916.
I. LANGMUIR. *Phys. Rev.*, **8**, 48–51, 1916 (Condensation Pump).
KNIPP. *Phys. Rev.*, **9**, 311, 1917, and **12**, 492, 1918.
RUSSELL. *Phys. Rev.*, **10**, 301, 1917.
BAKER. *Phys. Rev.*, **10**, 642, 1917.
SHRADER and SHERWOOD. *Phys. Rev.*, **12**, 70, 1918.
CRAWFORD. *Phys. Rev.*, **10**, 557, 1917.

KRAUS. *J. Amer. Chem. Soc.*, **39**, 2183, 1917.
STIMSON. *J. Wash. Ac. Sci.*, **7**, 477, 1917.
S. DUSHMANN. *Gen. Elect. Rev.*, **23**, 605–614 and 672–683, 1920.

II.—MANOMETERS

LORD RAYLEIGH. *Phil. Trans.*, **196** A., 205, 1901.
SHRADER and RYDER. *Phys. Rev.*, **13**, 321, 1919.
SCHEELE and HEUSE. *Zeits. f. Instrumentenkunde*, **29**, 14, 1909.
GUICHARD. *Ann. de Chim.*, **6**, 287–293, 1916.
SCHEELE and HEUSE. *Ber. d. deutsch. physik. Gesel.*, **10**, 785, 1908, and **11**, 10, 1909.
GAEDE. *Ann. d. Phys.*, **41**, 289, 1913.
A. FRESNEL. *Œuvres*, **2**, 667–672.
M. KNUDSEN. *Ann. d. Phys.*, **32**, 809–842, 1909.
G. W. TODD. *Phil. Mag.*, **38**, 381–382, 1919.
G. D. WEST. *Proc. Phys. Soc.*, **27**, 259, 1916; **31**, 278, 1919; **32**, 166, 1920; **32**, 222, 1920.
L. DUNOYER. Les Idées modernes sur la constitution de la Matière, *Soc. de Phys.*, p. 242, 1912.
ANGERER. *Ann. d. Phys.*, **41**, 1, 1913.
WOODROW. *Phys. Rev.*, **4**, 491, 1914.
SHRADER and SCHERWOOD. *Phys. Rev.*, **12**, 70, 1918.
M. KNUDSEN. *Ann. d. Phys.*, **44**, 525–536, 1914.
LEWIS F. RICHARDSON. *Proc. Phys. Soc.*, **31**, 270–277, 1919.
M. KNUDSEN. *Ann. d. Phys.*, **34**, 593, 1911.
SODDY and BERRY. *Proc. Roy. Soc.*, **84**, 576, 1911.
PIRANI. *Verh. d. deutsch. physik. Gesel.*, **24**, 684–694, 1906.
C. F. HALE. *Trans. Amer. Electrochem. Soc.*, **20**, 243–258, 1911.
N. R. CAMPBELL. *Proc. Phys. Soc.*, **33**, 287–296, 1921.
O. E. BUCKLEY. *Proc. Nat. Ac. Sci.*, **2**, 683, 1916.
MISAMICHI SO. *Proc. Physico-Math. Soc. Japan.*, **1**, 76, 1919.
S. DUSHMAN and C. G. FOUND. *J. Frank. Institute*, **188**, 819, 1919, and *Phys. Rev.*, **17**, 7–19, 1921.
KUNDT and WARBURG. *Pogg. Ann.*, **155**, 340, 1875.
SUTHERLAND. *Phil. Mag.*, **43**, 83, 1897.
HOGG. *Proc. Amer. Ac. Sci.*, **42**, 115, 1906.
SHAW. *Proc. Phys. Soc.*, **29**, 171, 1917.
M. KNUDSEN. *Ann. d. Phys.*, **46**, 641–656, 1915.
—— *Ann. d. Phys.*, **34**, 593, 1911.
I. LANGMUIR. *Phys. Rev.*, **1**, 337, 1913.
S. DUSHMAN. *Phys. Rev.*, **5**, 212–229, 1915.
I. LANGMUIR. *J. Amer. Chem. Soc.*, **35**, 105–127, 1913.
HABER and KERSCHBAUM. *Zeits. f. Elektrochem.*, **20**, 296, 1914.
S. DUSHMAN. *Gen. Elect. Rev.*, **23**, 731–740 and 847–856, 1920.

III.—TUBE SYSTEMS. OCCLUDED GASES. THE MICROANALYSIS OF GASES

M. KNUDSEN. *Ann. d. Phys.*, **28**, 75–130, 1909.
S. DUSHMAN. *Gen. Elect. Rev.*, **23**, 493–502, 1920.

C. Neumann. *Ber. d. König. Sächs. Gesel. d. Wiss. Math. Phys.*, **24,** 49, 1872.

Feddersen. *Pogg. Ann.*, **148,** 302, 1873.

Osborne Reynolds. *Phil. Trans.*, p. 727, 1879.

Cl. Maxwell. *Phil. Trans.*, p. 231, 1879.

M. Knudsen. *Ann. d. Phys.*, **31,** 205–229 and 633–640, 1910.

Clément and Rivière. *La Cellulose.*

L. Dunoyer. *Ann. de Physique,* **27,** 494–543, 1912.

Fuller. *Gen. Elect. Rev.*, **23,** 702–711, 1920.

W. Wilson. *Electrical Communication*, pp. 15–21, Aug. 1922.

M. Guichard. *Ann. de Chimie.*, **6,** 315–318, 1916, and *Bulletin de la Soc. Chim. de France*, **11,** 921, 1912.

I. Langmuir. *J. Amer. Chem. Soc.*, **38,** 2283 onwards, 1916.

—— *J. Amer. Chem. Soc.*, **38,** 2221–2295, 1916, and **39,** 1848–1906, 1917.

—— *Phys. Rev.*, **2,** 450, 1913.

S. Dushman. *Phys. Rev.*, **4,** 121, 1914.

Sherwood. *J. Amer. Chem. Soc.*, **40,** 1645, 1918, and *Phys. Rev.*, **12,** 448, 1918.

Shrader. *Phys. Rev.*, **13,** 434, 1919.

I. Langmuir. *J. Amer. Chem. Soc.*, **40,** 1361–1403, 1918.

M. Guichard. *Ann. de Chimie*, **6,** 285–317, 1918.

I. Langmuir. U.S. Patent No. 994,010, May 1911, and U.S. Patent No. 1,273,629, July 1918.

G. A. Hulett. *J. Amer. Chem. Soc.*, **42,** 1408, 1920.

Bancroft. *J. Frank. Institute*, **185,** 29, 1918.

Smith. *J. Physical Chem.*, **23,** 186, 1919.

F. G. Keyes. *J. Amer. Chem. Soc.*, **34,** 779, 1913.

Briggs. *J. Physical Chem.*, **9,** 617, 1905.

Katz. *Proc. Acad. Amsterdam*, **15,** 445, 1912.

I. Langmuir. *J. Amer. Chem. Soc.*, **35,** 105–127, 1913.

Ryder. *J. Amer. Chem. Soc.*, **40,** 1656–1662, 1918.

I. Langmuir. *J. Amer. Chem. Soc.*, **34,** 1310–1325 (1310 and 1313), 1912.

Ph. A. Guye and Germann. *J. de Chimie-Physique*, **14,** 194–203, 1916.

Research Staff of the General Electric Co., London. *Proc. Phys. Soc.*, **33,** 287–296, 1921.

IV.—PRODUCTION AND IMPROVEMENT OF VACUA BY ABSORBERS AND ELECTRIC DISCHARGES. CHEMICAL REACTIONS AT VERY LOW PRESSURES

J. Dewar. *Nature*, 15th July 1875 ; *Proc. Roy. Soc.*, **74,** 122 and 127, 1904, and *Encyclop. Britan.*, **16,** 751, 1912.

W. Travers. *Proc. Roy. Soc.*, **78,** 9, 1907.

McBain. *Phil. Mag.*, **18,** 916, 1909.

L. Vegard. *Ann. d. Physik.*, **50,** 169, 1916.

The Research Staff of the General Electric Co., London. *Phil. Mag.*, **40,** 585–611, 1920; **41,** 685–706, 1921; **42,** 227–246, 1921; **43,** 914–937, 1922.

V. CONTACT OF GASES WITH SOLID AND LIQUID BOUNDARIES. CONDENSATION, EVAPORATION, ADSORPTION, ACCOMMODATION COEFFICIENTS.

HERTZ. *Ann. d. Phys.*, **17**, 177, 1882.

M. KNUDSEN. *Ann. d. Phys.*, **47**, 697–708, 1915; **48**, 1113–1121, 1915; **50**, 472–488, 1916.

L. DUNOYER. *Comptes rendus*, **152**, 593, 1911, and *Radium*, **8**, 142, 1911; *Comptes rendus*, **157**, 1068–1070, 1913, and *Radium*, **10**, 400–402, 1913 ; *Les Gaz ultra-raréfiés*, see above, Chapter II.

R. W. WOOD. *Phil. Mag.*, **30**, 300–315, 1915.

O. STERN. *Zeits. f. Physik.*, **2**, 49–56, 1920, and **3**, 417–421, 1920.

I. LANGMUIR. *Phys. Rev.*, **2**, 329–342, 1913.

—— and MACKAY. *Phys. Rev.*, **4**, 377–386, 1914.

—— *Phys. Rev.*, **8**, 149–176, 1916.

—— *Proc. Nat. Ac. Sci.*, **3**, 141–147 and 251–257, 1917.

SMOLUCHOWSKI. *Phil. Mag.*, **46**, 199, 1898.

GAEDE. *Ann. d. Phys.*, **41**, 289, 1913.

TIMIRIAZEFF. *Ann. d. Phys.*, **40**, 97, 1913.

BAULE. *Ann. d. Phys.*, **44**, 145, 1914.

MILLIKAN. *Amer. Phys. Soc.* (Nov. 1918).

M. KNUDSEN. *Ann. d. Phys.*, **50 ?, 4**, 472, 1916; **52**, 105–108, 1917.

VOLMER. *Zeits. f. Phys.*, **5**, 31–33, 1921.

GROSS and VOLMER. *Zeits. f. Phys.*, **5**, 188–191, 1921.

VOLMER and ESTERMAN. *Zeit. f. Phys.*, **7**, 1–12, 1921, and **7**, 13–17, 1921.

J. WEISSENHOFF. *Ann. d. Phys.*, **58**, 505–514, 1919.

I. LANGMUIR. *J. Amer. Chem. Soc.*, **38**, 2221–2295, 1916; **40**, 1361–1403, 1918.

S. DUSHMAN. *Gen. Elect. Rev.*, **24**, 810–819 and 890–901, 1921.

G. CLAUDE. *Comptes rendus*, **158**, 861, 1914.

TITOFF. *Zeits. Physik. Chemie*, **74**, 641, 1910.

HOMFRAY. *Zeits. Physik. Chemie*, **74**, 129, 1910.

BAERWALD. *Ann. d. Phys.*, **23**, 84, 1907.

BERGTER. *Ann. d. Phys.*, **37**, 472, 1912.

DORSEY. *J. Ind. and Eng. Chem.*, **11**, 281, 1919.

LEMON. *Phys. Rev.*, **14**, 281–293, 1919.

—— and K. BLODGETT. *Phys. Rev.*, **14**, 394–403, 1919.

R. E. WILSON. *Phys. Rev.*, **16**, 8, 1920.

SHELDON. *Phys. Rev.*, **16**, 165, 1920.

S. DUSHMAN. *Gen. Elect. Rev.*, **24**, 58–68, 1921.

VALENTINER. *Verh. d. deut. physik. Gesel.*, **3**, 1003, 1911.

F. SODDY. *Proc. Roy. Soc.*, **78**, 429, 1907.

NORMAN PILLING. *Phys. Rev.*, **18**, 362–368, 1921.

MATIGNON and DELÉPINE. *Comptes rendus*, **131**, 837, 1900.

MATIGNON. *Comptes rendus*, **131**, 891, 1900.

MALLET. *Amer. J. Science*, **28**, 346, 1859.

COOLIDGE. U.S. Patent No. 1,323,836 (2nd Dec. 1919).

I. LANGMUIR. *J. Amer. Chem. Soc.*, **34**, 860–877, 1912 ; **34**, 1310–1325, 1912 ; **35**, 105–127, 1913 ; **35**, 931–945, 1913 ; **36**, 1708–1722, 1914 ; **37**, 417–458, 1915 ; **37**, 1139–1167, 1915 ; **38**, 1145–1156, 1916 ; **41**, 167–194, 1919.

FREEMAN. *J. Amer. Chem. Soc.*, **35**, 927–931, 1913.
DUSHMAN. *Gen. Elect. Rev.*, **34**, 436–444, 1921.
CLOUGH. U.S. Patent No. 1,246,054 (1917).
J. MACKAY. U.S. Patent No. 1,208,597, 1917, and No. 1,249,978, 1917.
DUSHMAN. *Gen. Elect. Rev.*, **34**, 669–681, 1921.
WHITNEY. *Trans. Amer. Inst. Elect. Eng.*, **31**, 921, 1912.
D. McRAE and VAN VOORHIS. *J. Amer. Chem. Soc.*, **43**, 547–553, 1921.
P. JOLIBOIS. *Comptes rendus*, **149**, 287, 1909, and **151**, 382, 1910.
NEWMAN. *Proc. Roy. Soc.*, **90**, 499–506, 1914.
—— *Proc. Phys. Soc.*, **32**, 190–195, 1920, and **33**, 73–82, 1921.
—— *Phil. Mag.*, **44**, 215–226, 1922.
W. C. KAYE. *X Rays*, chapter vi.
WILLOWS. *Phil. Mag.*, **6**, 503, 1901.
MEY. *Ann. d. Phys.*, **11**, 127, 1903.
SKINNER. *Phil. Mag.*, **12**, 481, 1906.
CHRISLER. *Phys. Zeits.*, **10**, 745, 1909.
CAMPBELL-SWINTON. *Proc. Roy. Soc.*, **79**, 134, 1907.
RIECKE. *Ann. d. Phys.*, **15**, 1103, 1904.
F. SODDY and MACKENZIE. *Proc. Roy. Soc.*, **80**, 92, 1908.
HILL. *Proc. Phys. Soc.*, **35**, 1912.

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